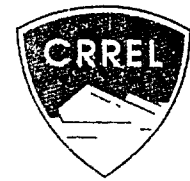


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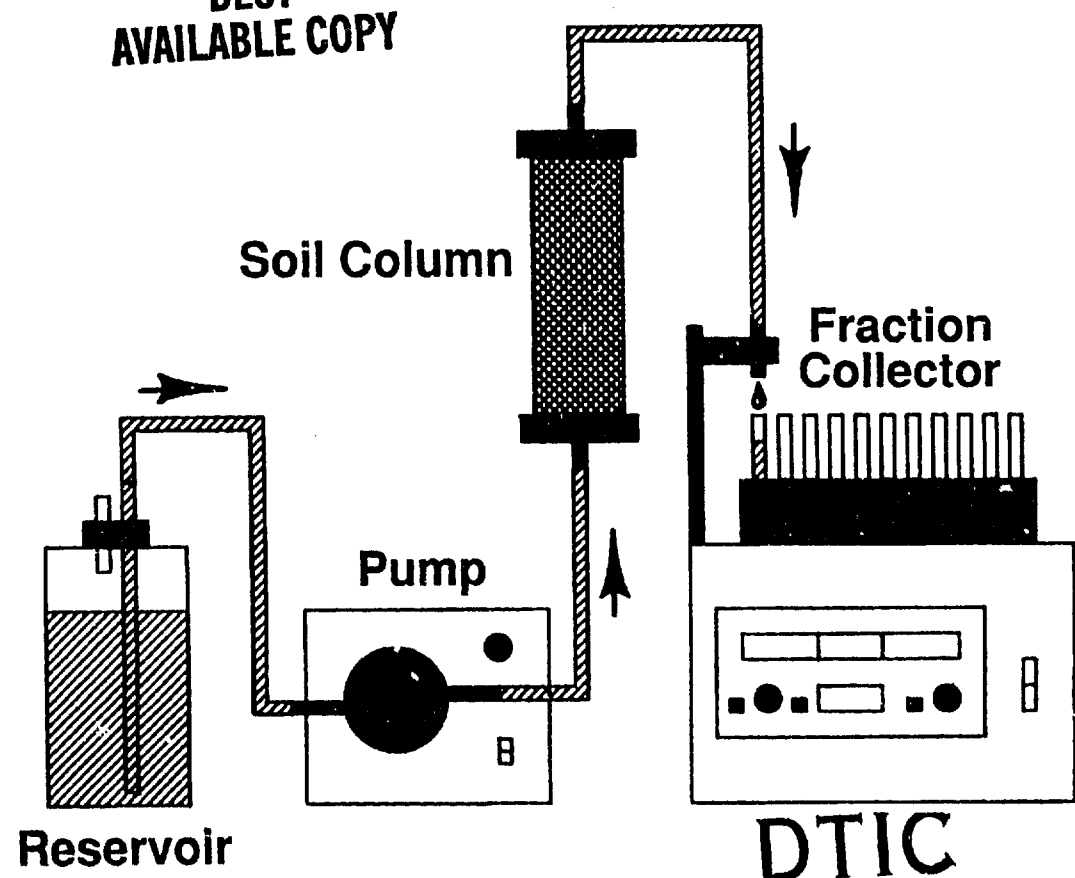
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Modeling the Transport of Heavy Metals in Soils

H.M. Selim, M.C. Amacher and I.K. Iskandar

September 1990

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Cover: The experimental design of the transport experiments.

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**U.S. Army Corps
of Engineers**
Cold Regions Research &
Engineering Laboratory

Modeling the Transport of Heavy Metals in Soils

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PREFACE

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NOMENCLATURE

<i>Term</i>	<i>Definition</i>
a	aggregate radius (cm)
b	Freundlich parameter (dimensionless)
c	concentration of dissolved chemical in soil solution (mg L^{-1})
c^m	heavy metal concentration in mobile phase (mg L^{-1})
c^{im}	heavy metal concentration in immobile phase (mg L^{-1})
C	dimensionless solute concentration in solution
C_i	initial solute concentration
C_o	applied (input) concentration in solution (mg L^{-1})
C/C_o	relative solute concentration
D	hydrodynamic dispersion coefficient ($\text{cm}^2 \text{hr}^{-1}$)
D^a	molecular diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
D^m	hydrodynamic dispersion coefficient in mobile water region ($\text{cm}^2 \text{hr}^{-1}$)
f^m	fraction of dynamic sites to total sites s_T (dimensionless)
F	fraction of type 1 sites to total sites (dimensionless)
H	sum of concentration and equilibrium sorbed phases
j	time step (known)
$j+1$	time step (unknown)
K_d	solute distribution coefficient ($\text{cm}^3 \text{kg}^{-1}$)
k_s	rate coefficient for irreversible reaction (hr^{-1})
k_1, k_2	forward and reverse rate coefficients (hr^{-1})
k_3, k_4	forward and reverse rate coefficients (hr^{-1})
L	thickness of soil profile (cm)
m	reaction order (dimensionless)
n	nonlinear parameter, reaction order (dimensionless)
p	number of parameters
P	Peclet number (dimensionless)
P^m	Peclet number for flow in the mobile water phase (dimensionless)
Q	irreversible rate of solute supply or removal from soil solution ($\text{mg cm}^{-3} \text{hr}^{-1}$)
Q^m	irreversible rate of supply or removal from mobile water phase ($\text{mg cm}^{-3} \text{hr}^{-1}$)
Q^{im}	irreversible rate of supply or removal from immobile water phase ($\text{mg cm}^{-3} \text{hr}^{-1}$)
i	iteration steps
rms	root mean square
rss	residual sum of squares
R	retardation factor
s	amount of solute retained per unit mass of soil matrix (mg kg^{-1})
s_e	amount of heavy metal sorbed in equilibrium phase (mg kg^{-1})
s^m	sorbed amount in dynamic region (mg kg^{-1})
s^{im}	sorbed amount in stagnant region (mg kg^{-1})

<i>Term</i>	<i>Definition</i>
s_{\max}	maximum sorption (mg kg^{-1})
s_T	total amount of sorption sites (mg kg^{-1})
s_1, s_2	amounts retained by type 1, 2 sites
S	relative amount of solute retained by soil (dimensionless)
$S_{\text{n-irr}}$	phases representing heavy metal retained by soil
S_T	total sites in soil matrix (mg kg^{-1})
t	time (hr)
t_p	duration of pulse (hr)
T	time (dimensionless)
T_p	duration of applied pulse (dimensionless)
v	Darcy's water flux density (cm hr^{-1})
V/V_o	pore volume of effluent (dimensionless)
x	soil depth (cm)
α	mass transfer coefficient (hr^{-1}) between mobile and immobile phases
ϕ	amount of vacant sites in the soil (mg kg^{-1})
ϕ^m	unfilled sites in dynamic region (mg kg^{-1})
ϕ^{im}	unfilled sites in stagnant region (mg kg^{-1})
κ_n	kinetic rate coefficients (dimensionless)
Θ	volumetric soil water content ($\text{cm}^3 \text{cm}^{-3}$)
Θ^m	mobile water content ($\text{cm}^3 \text{cm}^{-3}$)
Θ^{im}	immobile water content ($\text{cm}^3 \text{cm}^{-3}$)
ρ	soil bulk density (g cm^{-3})
u	pore water velocity (v/Θ^m)
ω_n	equilibrium constants for retention reactions
Ω	dimensionless parameter

Modeling the Transport of Heavy Metals in Soils

H.M. SELIM, M.C. AMACHER AND I.K. ISKANDAR

Chapter 1. Introduction

Retention reactions in soils are important processes that govern the fate of chemical contaminants such as heavy metals in groundwaters. The ability to predict the mobility of heavy metals in the soil and the potential contamination of groundwater supplies is a prerequisite in any program aimed at protecting groundwater quality. Mathematical models that describe the potential mobility of heavy metals must include description of the retention processes in the soil matrix.

Extensive research has been carried out to describe the retention–release behavior of several heavy metals in soils. Fuller (1977), Alesii et al. (1980), Dowdy and Volk (1983), Ellis et al. (1983), and Kabata-Pendias and Pendias (1984), among others, have presented overviews of retention–release and leaching investigations for several heavy metals in soils. These publications also describe soil physical and chemical properties that influence the fate of heavy metals in the soil environment and their potential leaching to groundwater supplies. Over the last two decades, however, only a limited number of investigations have attempted to quantify the mobility of heavy metals in the soil profile. Specifically, mathematical models that describe the transport of heavy metals in laboratory soil columns or in soil profiles under field conditions have only recently appeared in the literature.

Sidle et al. (1977) were among the earliest researchers to utilize the convection–dispersion equation for the description of Cu, Zn, and Cd movement in a sludge-treated forest soil. The primary feature of their model is that the retention–release mechanism was assumed to be fully reversible and of the nonlinear equilibrium (Freundlich) type. Model calculations resulted in underprediction of the mobility of these metals at two depths. A similar approach was used by Amoozegar-Fard et al. (1983) and van Genuchten and Wierenga (1986), where a linear equilibrium sorption mechanism was incorporated into the convection–dispersion equation to describe Cr(VI) mobility in soil columns. Recently, Schmidt and Sticher (1986) found that the equilibrium retention of cadmium, lead, and copper was successfully described by a two-site sigmoidal Langmuir isotherm equation.

For several heavy metals (e.g., Cu, Hg, Cr, Cd, and Zn), retention–release reactions in the soil solution have been observed to be strongly time-dependent. Recent studies on the kinetic behavior of the fate of several heavy metals include Harter (1984), Aringhieri et al. (1985), and Amacher et al. (1986), among others. A number of empirical models have been proposed to describe kinetic retention–release reactions of solutes in the solution phase. The earliest model is the first-order kinetic equation that was first incorporated into the convection–dispersion transport equation by Lapidus and Amundson (1952). First-order kinetic reactions have been extended to include the nonlinear kinetic type (van Genuchten et al. 1974, Mansell et al. 1977, Fiskell et al. 1979). A variety of other kinetic reactions are given by Murali and Aylmore (1983). Amacher et al. (1986) found that the use of single-reaction kinetic models did not adequately describe the time-dependent retention of Cr, Hg, and Cd for several initial concentrations and several soils. As a result Amacher et al. (1988) developed a multireaction model that includes concurrent and concurrent–consecutive processes of the nonlinear kinetic type. The model was capable of describing the retention behavior of Cd and Cr(VI) with time for several soils. In addition, the model predicted that a fraction of these heavy metals was irreversibly retained by the soil. A literature search revealed that no studies were carried out on the description of heavy metals transport in soils where the retention–release reactions are based on kinetic mechanisms. The study of Amoozegar-Fard et al. (1984) is perhaps the first study to investigate the mobility of Cd, Ni, and Zn using a fully reversible first-order kinetic reaction.

The failure of single-reaction models (e.g. Freundlich and Langmuir) to describe the retention and particularly the slow release of several solutes resulted in the development of a number of multireaction (multisite) models based on multiple retention–release reactions, which may be of the equilibrium or time-dependent types. The two-site Langmuir model is one of the earliest multisite models. A derivation and proposed use of this model was given by Sposito (1982). As an alternative, an equilibrium–kinetic two-site model was proposed by Selim *et al.* (1976). The success of the two-site approach leads us to believe that a more universal multireaction (multisite) model is plausible.

SCOPE OF THE MONOGRAPH

The scope of this monograph is to present an overview of the retention of heavy metals in soils and methods of modeling their transport based on the classic approach of the convection–dispersion equation. This chapter describes widely used solute-retention models with emphasis on solute-retention mechanisms characterized by time-dependent (or kinetic) and nonlinear-type reactions. Chapter 2 gives retention properties based on equilibrium (Freundlich)-type sorption for several heavy metals by a number of soil orders.

In subsequent chapters, we present four general-purpose multireaction, multisite, kinetic-type models for describing the behavior of heavy-metal retention and mobility in soils; namely the MRM, MRTM, SOTS model, and SOMIM. These models are discussed in detail in Chapters 3, 7, and 8, respectively. Briefly, the major features of each model are as follows:

- **MRM**—A multireaction model that includes concurrent and concurrent–consecutive retention processes of the nonlinear kinetic type. It accounts for equilibrium (Freundlich) sorption as well as irreversible reactions. The processes considered here are based on linear (first-order) and nonlinear kinetic reactions. The MRM is capable of describing heavy metals under batch (kinetic) conditions where water flow is not considered.
- **MRTM**—A multireaction and transport model that represents an extension of MRM, with the retention processes incorporated into the convection–dispersion equation for solute transport in soils under steady water flow.
- **SOTS**—A second-order kinetic approach for describing solute retention during transport in soils. This approach accounts for the sites on the soil matrix that are accessible for retention of the reactive solutes in solution. One can assume that these processes are predominantly controlled by surface reactions of adsorption and exchange. The second-order reactions associated with the two sites may be considered as kinetically controlled, heterogeneous chemical retention reactions.
- **SOMIM**—An extension of the second-order model of the diffusion–controlled mobile–immobile or two-region concept. Specifically, we consider the processes of retention to be controlled by two types of reactions: namely, a chemically controlled heterogeneous reaction and a physically controlled reaction. The first is governed according to the second-order approach, whereas the latter is described by diffusion or mass transfer of the mobile–immobile concept. Irreversible reaction of the first-order kinetic type was also incorporated in the transport model.

Computer codes and sample input/output runs from each of these models are given in the appendixes. In addition, validation of the above models based on selected studies are given in Chapters 4, 5, 6, and 9.

EQUILIBRIUM RETENTION MODELS

It is well accepted that, under steady water flow conditions, transport of dissolved chemicals in soils is governed by the following convection–dispersion transport equation (Brenner 1962):

$$\rho \partial s / \partial t + \Theta \partial c / \partial t = \Theta D \partial^2 c / \partial x^2 - v \partial c / \partial x - Q \quad (1-1)$$

where c = concentration of the dissolved chemical in the soil solution (mg L^{-1})

- s = amount of solute retained per unit mass of the soil matrix (mg kg^{-1})
- D = hydrodynamic dispersion coefficient ($\text{cm}^2 \text{ day}^{-1}$)
- v = Darcy's water flux (cm hr^{-1})
- Θ = volumetric soil moisture content ($\text{cm}^3 \text{ cm}^{-3}$)
- ρ = soil bulk density (g cm^{-3})
- t = time (hr)
- x = soil depth (cm).

The two terms on the right-hand side of eq 1-1 are commonly known as the dispersion and convection terms, respectively. The term $\partial s/\partial t$ represents the rate for reversible solute removal from the soil solution. In contrast, the term Q is a source or a sink representing irreversible solute production (Q negative) or solute removal (Q positive) from the soil solution ($\text{mg cm}^{-3} \text{ hr}^{-1}$).

Over the last two decades, several analytical models for the description of solute transport in porous media have been proposed. One group of models deals with solute transport in well-defined geometrical systems of pores and/or cracks of regular shapes or interaggregate voids of known geometries. Examples of such models include those of Rasmuson and Neretnieks (1980) for uniform spheres, Tang et al. (1981) for rectangular voids, van Genuchten et al. (1984) for cylindrical voids, and Rasmuson (1985) for discrete aggregate or spherical size geometries. van Genuchten and Dalton (1986) provided a review of models utilizing such an approach. Solutions of these models are analytic, often complicated, and involve several numerical approximating steps. Recent applications include transport in fixed beds consisting of spheres or aggregates (Nkedi-Kizza et al. 1984, Goltz and Roberts 1986). Another group of transport models that are widely used are those that do not consider well-defined geometries of the pore space or soil aggregates. Rather, solute transport is treated on a macroscopic basis with ρ , Θ , v , and D of eq 1-1 as the associated parameters that describe the transport processes in the bulk soil. The "mobile-immobile" transport models are refinements of this macroscopic approach. Here, it is assumed that soil-water is divided into two regions. One is a mobile-water region that is considered to be present in large pores and through which solute transport occurs by convection and mechanical dispersion. The other is an immobile-water region present in the bulk matrix and through which relatively little or no water flows. Mobile-immobile models have been introduced by Coats and Smith (1964), Skopp and Warrick (1974), van Genuchten and Wierenga (1976), and Skopp et al. (1981). The mobile-immobile models have been extensively used to describe several solutes (for a review, see Nielsen et al. 1986).

Description of the solute retention mechanisms as expressed by the term $\partial s/\partial t$ has been the focus of investigators for several years. Such a description, when incorporated into eq 1-1, provides a predictive tool for the transport of dissolved chemicals in the soil profile. Most mathematical models that describe the retention mechanisms are based on the validity of the local equilibrium assumption (LEA) in the soil system (Rubin 1983). Here it is assumed that the reaction of an individual solute species in the soil is sufficiently fast or instantaneous and that an "apparent equilibrium" condition may be observed in a few minutes or hours. Such a behavior has been used as the basis for soil surface adsorption mechanisms as well as ion-exchange reactions. For a review see Travis and Etnier (1981), Murali and Aylmore (1983), and Amacher et al. (1986). Linear, Freundlich, and Langmuir sorption models are perhaps the most commonly used equilibrium-type models for describing the retention of a wide range of dissolved chemicals in soils. A partial listing of equilibrium type models is given in Table 1-1. The linear and Freundlich models utilize the solute distribution coefficient (K_d), which partitions the solute between that in the soil solution and the amount sorbed by the soil matrix. A discussion of the K_d parameter and its capability for describing contaminant migration is given by Reardon (1981). Unlike the Langmuir models, linear and Freundlich models do not include a maximum sorption term (s_{max}). This is a disadvantage since the capacity of the soil for solute removal, i.e., the total sites, is finite and should be an important limiting factor. Langmuir models are perhaps the most widely used equilibrium models for describing the fate of solutes such as phosphorus and heavy metals in soil (Larson 1967, Amacher et al. 1988). The two-site Langmuir model may be considered as one of the earliest multireaction-type models. Here one assumes complete equilibrium and partitions the reaction sites into two fractions. Holford et al. (1974) were one of the earliest researchers to evaluate this model for describing P retention by several soils. Recently, the two-site Langmuir was modified

Table 1-1. Selected equilibrium and kinetic type models for solute retention in soils.

<i>Model</i>	<i>Formulation</i>
Equilibrium type	
Linear	$s = K_d c$
Freundlich (nonlinear)	$s = K_d c^n$
Langmuir	$s = b c s_{\max} / (1 + bc)$
Langmuir with sigmoidicity	$s = b c s_{\max} / (1 + bc + k'c)$
Kinetic type	
First-order	$\partial s / \partial t = k_1 (\Theta/\rho) c - k_2 s$
<i>n</i> th order	$\partial s / \partial t = k_1 (\Theta/\rho) c^n - k_2 s$
Irreversible (sink/source)	$\partial s / \partial t = k_s (\Theta/\rho) (c - c_p)$
Langmuir kinetic	$\partial s / \partial t = k_1 (\Theta/\rho) c (s_{\max} - s) - k_2 s$
Elovich	$\partial s / \partial t = A \exp(-Bs)$
Power	$\partial s / \partial t = k (\Theta/\rho) c^n s^m$
Mass transfer	$\partial s / \partial t = k (\Theta/\rho) (c - c^*)$

to incorporate the sigmoidal shape of Cu, Pb, and Cd sorption isotherms observed at extremely low concentrations (Schmidt and Sticher 1986). The equilibrium models given in Table 1-1 have been used to describe adsorption isotherms for a wide range of heavy metal species and organics (Travis and Etnier 1981, Amacher et al. 1988).

Other types of equilibrium models are those based on ion-exchange reactions (Rubin and James 1973, Valocchi et al. 1981). Unlike previous models, which are empirical in nature, ion-exchange models are based on rigorous thermodynamics where the reaction stoichiometry is explicitly considered. A set of recursion formulas has been formulated by Rubin and James (1973) that describe exchange isotherms for multiple ions in the soil. Recently, aqueous equilibrium reactions, along with ion-exchange reactions, have been used to describe multiple-ion transport in soils (Jennings et al. 1982, Miller and Benson 1983). Ion exchange has been used by several researchers to describe the transport of ions, including Na, Ca, Mg, Zn, Li, Cs, and Cd, in the soil solution (Valocchi et al. 1981, Persaud and Wierenga 1982, Cederberg et al. 1985).

KINETIC MODELS

It has been observed that the amount of solute retained (or released) from the soil solution may be strongly time-dependent. Several models have been proposed to describe the kinetic reactions of dissolved chemicals in the soil solution. Most common is the first-order kinetic reaction, which was incorporated into the convection-dispersion transport equation by Lapidus and Amundson (1952). Such reactions are assumed to be fully reversible, and the magnitude of the reaction coefficients determines the time when apparent equilibrium may be attained. The first-order kinetic model has been modified to account for the nonlinear kinetic behavior of retention mechanisms. Such a modified model was used successfully to describe the retention of heavy metals in batch and miscible displacement studies (Harter 1984, Aringhieri et al. 1985, Amacher et al. 1986, 1988). Another fully reversible model is that of the Langmuir kinetic type (see Table 1-1), which is nonlinear and includes a maximum retention capacity term (Rubin 1983). A discussion of the kinetic behavior of the Langmuir sorption reaction mechanisms during transport is presented by Jennings and Kirkner (1984).

Another type of kinetic model is the two-site model proposed by Selim et al. (1976) and Cameron and Klute (1977). This model was developed to describe observed batch results that showed rapid initial retention reac-

tions followed by slower reactions. The model was also developed to describe the excessive tailing of breakthrough results obtained from pulse inputs in miscible displacement experiments. Single retention models of the first- and n th-order kinetic type consistently failed to describe such batch or miscible displacement results. The two-site model is based on several simplifying assumptions. It is assumed that a fraction of the total sites (referred to as type 1 sites) are highly kinetic in nature. As a result, type 1 sites were assumed to react slowly with the solute in the soil solution. In contrast, we consider type 2 sites to react rapidly with the soil solution. The retention reactions for both types of sites were based on the nonlinear (or n th-order) reversible kinetic approach outlined in Table 1-1. The convection-dispersion transport equation with the two-site retention mechanism may be expressed as

$$\Theta \partial c / \partial t = \Theta D \partial^2 c / \partial x^2 - v \partial c / \partial x - (k_1 \Theta c^n - k_2 \rho s_1) - (k_3 \Theta c^m - k_4 \rho s_2) \quad (1-2)$$

$$\partial s_1 / \partial t = k_1 (\Theta / \rho) c^n - k_2 s_1 \quad (1-3)$$

$$\partial s_2 / \partial t = k_3 (\Theta / \rho) c^m - k_4 s_2 \quad (1-4)$$

where

$$s_T = s_1 + s_2 \quad (1-5)$$

where s_1 and s_2 are the amounts retained by type 1 and 2 sites, respectively, and s_T is the total amount of solute retained. The nonlinear parameters m and n are usually considered less than unity and $n \neq m$. For the case $n = m = 1$, the retention reactions are of the first-order type, and the problem becomes a linear one.

This two-site approach was also considered for the case when type 2 sites are assumed to be in equilibrium with the soil solution. Such conditions may be attained when the values for the forward and backward (or k_3 and k_4) rate coefficients are extremely large in comparison to the water flow velocity (v). That is, the local equilibrium assumption is valid for type 2 sites (Valocchi 1985). Under these conditions, the solute convection-dispersion transport equation for a combined model of equilibrium and kinetic retention is (Selim et al. 1976)

$$R \partial c / \partial t = D \partial^2 c / \partial x^2 - v \partial c / \partial x - [k_1 c^n - k_2 (\rho / \Theta) s_1] \quad (1-6)$$

$$R = 1 + (\rho / \Theta) K_d m c^{m-1} \quad (1-7)$$

and

$$s_2 = K_d c^m \quad (1-8)$$

where eq 1-7 and 1-8 describe a Freundlich-type equilibrium reaction. The term R of eq 1-7 is the retardation factor, which for this nonlinear case is a function of c . The two-site model has been used by several scientists, including De Camargo et al. (1979), Rao et al. (1979), Hoffman and Rolston (1980), Nkedi-Kizza et al. (1984), Jardine et al. (1985), and Parker and Jardine (1986). It proved successful in describing the retention and transport of several dissolved chemicals including Al, 2,4-D, atrazine, P, K, Cd, Cr, and methyl bromide.

The two-site model described above may be considered as a multireaction model since more than a single reaction and/or sorbed species of the solute were considered. However, the two-site model is restricted to fully reversible mechanisms and it does not account for possible consecutive-type solute interactions in the soil system. Mansell et al. (1977) proposed a first-order irreversible kinetic process to describe possible precipitation of phosphorus in miscible displacement studies. Recently, Amacher et al. (1986, 1988) showed that the sink term was necessary to describe batch results for Hg, Cd, and Cr retention vs time for five different soils. This sink term is similar to that for diffusion-controlled precipitation reactions if one assumes that the equilibrium concentration for precipitation is negligible and that k_s is related to the diffusion coefficient. Among kinetic

models that are used to describe the rate of irreversible reactions is the Elovich model given in Table 1-1. For further discussion of irreversible kinetic models, see Travis and Etnier (1981) and Selim (1989).

Models that account for reversible as well as irreversible processes of solutes in the soil environment (i.e., multireaction models) may be regarded as simplified versions of multicomponent models that account for chemical and/or biological reactions of the sequential and concurrent type. Examples of these reactions include precipitation/dissolution, mineralization, immobilization, biological transformations, and radioactive decay, among others. Models that account for first-order kinetic decay reactions include those of Rasmuson (1985) and van Genuchten (1985). Other, more complex, models are those based on ion-exchange reactions for multiple ions along with chemical equilibrium reactions in the soil solution. Examples of such models include those of Jennings et al. (1982), Miller and Benson (1983), and Cederberg et al. (1985). There are several advantages in utilizing such models since they are flexible and can be adapted to incorporate other processes as deemed appropriate. The governing reactions may be kinetic or equilibrium in nature. Furthermore, these models are not restricted to a specific number of solute species with either concurrent or consecutive reactions.

A prerequisite for the adoption of a multireaction model as a predictive tool, however, is that it must be validated for a specific contaminant and the conditions under consideration. To carry out complete validation of such a model often requires extensive laboratory evaluation of necessary model parameters. The dependence of model parameters on other variables such as pH, temperature, and redox potential must be determined. The model must also be evaluated for a range of soils with different physical and chemical properties.

When rigorous validation of the model is not possible, a partial validation based on a limited data set obtained in the laboratory is necessary. After laboratory validation, the model should be tested with data sets obtained from controlled field experiments. Field evaluation often results in several modifications of the model. In some cases, it may be desirable to have more than one model version, with each applicable to a specified set of conditions. Although it is often recognized that data sets that are suitable for model validation may not be available, it is essential that partial model validation be performed.

Chapter 2. Heavy Metals Retention in Soils: A Simplified Approach

For many years, potentially harmful substances have been added to soils through land application of agricultural chemicals, industrial wastewater and sludge disposal, landfills, and leaking hazardous waste storage sites. The potentially harmful substances, including heavy metals, pesticides and other industrial organic chemicals, and even plant nutrient supplements, may contaminate soils, surface water bodies, and subsurface aquifers. Thus, concern about soil and water quality has led to an increased interest in understanding the processes of solute reactions and transport in soils.

To predict the transport of these solutes, models that include retention and release reactions of solutes with the soil matrix are needed. Retention and release reactions in soils include precipitation/dissolution, ion exchange, and adsorption/desorption reactions (Amacher et al. 1986). Retention and release are influenced by a number of soil properties including texture, bulk density, pH, Eh, organic matter, and type and amount of clay minerals. Adsorption is the process whereby solutes bind to surfaces of soil particles to form outer- or inner-sphere solute-surface site complexes; ion exchange is the process whereby charged solutes replace ions on soil particles. Adsorption and ion exchange are related in that an ionic solute species may form a surface complex and may replace another ionic solute species already on the surface binding site. Strictly speaking, the term *retention* or the commonly used term *sorption* should be used when the mechanism of solute removal from solution in soil is not known, and the term *adsorption* should be used only to describe the formation of solute-surface site complexes. However, *sorption* is often used to include all processes mentioned above, even though the processes in most experiments cannot be distinguished.

Solute retention and release by soil matrix surfaces are described by equilibrium models and by kinetic or time-dependent models. Equilibrium-type models assume rapid or instantaneous reactions of the solute with the soil matrix. Common approaches are Langmuir-type models with a maximum sorption term and linear and nonlinear Freundlich-type models without a maximum sorption term. Kinetic models describe retention and release as a function of time and include irreversible and reversible 1st-, 2nd-, and n th-order models. However, the ability of a particular model to describe data does not reveal the actual nature of the retention process (Sposito 1984, Skopp 1986).

A SIMPLIFIED APPROACH

The Freundlich equation is perhaps the simplest approach for quantifying the behavior of heavy metals in soils. It is certainly one of the oldest of the nonlinear sorption equations and has been used widely to describe solute retention by soils (Helfferich 1962, Sposito 1984, Travis and Etnier 1981, Murali and Aylmore 1983). The nonlinear Freundlich equation is

$$S = K_d c^b \quad (2-1)$$

where S is the amount of solute retained by the soil (mg kg^{-1}), c is the solute concentration in solution (mg L^{-1}), K_d is the distribution coefficient ($\text{cm}^3 \text{ kg}^{-1}$), and parameter b is dimensionless and typically has a value of $b < 1$. The distribution coefficient describes the partitioning of a solute species between solid and liquid phases over the concentration range of interest and is analogous to the equilibrium constant for a chemical reaction.

Although the Freundlich equation has been rigorously derived (Sposito 1980), its goodness-of-fit to solute retention data does not provide definitive information about the actual processes involved, since the equation is capable of describing data irrespective of the actual retention mechanism. Complex retention processes can often be described at least in part by relatively simple models such as the Freundlich equation. Therefore, the Freundlich parameters K_d and b are best regarded as descriptive parameters in the absence of independent evidence concerning the actual retention mechanism.

An extensive body of literature describes the retention of various elements by soils (e.g., see the review by Travis and Etmer [1981]). In most cases the retention of a single element by a few soils is the subject of a given study (e.g., Goldberg and Glaubig 1986). Some researchers, such as Harter (1983), have compared retention of different elements. Korte et al. (1976) applied 11 trace elements to 11 soils from 7 soil orders and compared qualitatively the relative mobilities of the trace elements. Comprehensive studies of the retention of several elements by widely divergent soils are, however, for the most part lacking.

In this chapter we quantify (using the Freundlich equation) and compare retention of 15 elements by 11 soils from 10 soil orders. We also relate retention parameters K_d and b to basic properties of the soils and elements. This simplified approach also provides characteristics of retention properties of elements for which data are seldom available as well as a database of retention parameters for future studies.

SOILS AND METHODS

Soils

The names, taxonomic classification, and selected properties of the 11 soils used in this study are listed in Table 2-1. The B21h horizon of the Spodosol and the Ap horizons of the other soils were used in the retention study. The soils were characterized by the Soil Testing and Soil Characterization Laboratories at Louisiana State

Table 2-1. Taxonomic classification and selected soil properties.

Soil*	Horizon	Taxonomic classification	pH	Sum of cations exch.				Percent						
				TOC (%)	CEC	OH	MnO ₂	Amor. Fe ₂ O ₃	Free Fe ₂ O ₃	Al ₂ O ₃	CaCO ₃	Sand	Silt	Clay
Alligator	Ap	Very-fine, montmorillonitic, acid, thermic Vertic Haplaquept	4.8	1.54	30.2	3.5	0.028	0.33	0.74	0.15	—	5.9	39.4	54.7
Unnamed	Ap	Calciorthid	8.5	0.44	14.7	33.8	0.015	0.050	0.25	0.000	7.39	70.0	19.3	10.7
Cecil	Ap	Clayey, kaolinitic, thermic Typic Hapludult	5.7	0.61	2.0	2.0	0.001	0.099	1.76	0.27	—	78.8	12.9	8.3
Cecil	B	Clayey, kaolinitic, thermic Typic Hapludult	5.4	0.26	2.4	6.6	0.002	0.082	7.48	0.94	—	30.0	18.8	51.2
Kula	Ap1	Medial, isothermic Typic Euthandept	5.9	6.62	22.5	82.4	0.093	1.68	5.85	3.51	—	73.7	25.4	0.9
Kula	Ap2	Medial, isothermic Typic Euthandept	6.2	6.98	27.0	58.5	0.13	1.64	6.95	3.67	—	66.6	32.9	0.5
Lafitte	Ap	Eucic, thermic Typic Medisaprism	3.9	11.6	26.9	4.7	0.009	1.19	1.16	0.28	—	60.7	21.7	17.6
Molokai	Ap	Clayey, kaolinitic, isohyperthermic Typic Torrox	6.0	1.67	11.0	7.2	0.76	0.19	12.4	0.91	—	25.7	46.2	28.2
Norwood	Ap	Fine-silty, mixed (calc.), thermic Typic Udifluent	6.9	0.21	4.1	0.0	0.008	0.061	0.30	0.016	—	79.2	18.1	2.8
Olivier	Ap	Fine-silty, mixed, thermic Aquic Fragiudalf	6.6	0.83	8.6	1.9	0.27	0.30	0.71	0.071	—	4.4	89.4	6.2
Unnamed	B21h	Spodosol	4.3	1.98	2.7	5.2	0.0	0.009	0.008	0.22	—	90.2	6.0	3.8
Webster	Ap	Fine-loamy, mixed, mesic Typic Haplaquoll	7.6	4.39	48.1	14.1	0.063	0.19	0.55	0.10	3.14	27.5	48.6	22.9
Windsor	Ap	Mixed, mesic Typic Udipsamment	5.3	2.03	2.0	10.2	0.041	0.42	1.23	0.56	—	76.8	20.5	2.8
Windsor	B	Mixed, mesic	5.8	0.67	0.8	10.1	0.031	0.23	0.79	0.29	—	74.8	24.1	1.1

* The states from which the soil samples originated are Louisiana (Alligator, Lafitte, Norwood, and Olivier soils), South Carolina (Cecil soil), Hawaii (Kula and Molokai soils), Iowa (Webster soil), New Hampshire (Windsor soil), New Mexico (Calciorthid), and Florida (Spodosol).

University. They were air-dried and passed through a 2-mm sieve before use. The following methods were used to identify the properties of the 11 soils:

- Soil pH was measured using a 1:1 soil–water suspension (McLean 1982).
- Total organic carbon (TOC) and carbonates were determined by wet combustion methods with gravimetric determination of CO_2 (Nelson 1982, Nelson and Sommers 1982).
- Cation exchange capacity (CEC) was determined by summing the exchangeable bases plus aluminum as determined by replacement with 0.1 M BaCl_2 – 0.1 M NH_4Cl .
- Exchangeable OH was determined by replacement with F ions (Perrott et al. 1976).
- MnO_2 and amorphous Fe_2O_3 were determined by extraction with 0.25 M $\text{NH}_2\text{OH-HCl}$ – 0.25 M HCl at 50°C (Chao and Zhou 1983).
- Free Fe_2O_3 and Al_2O_3 were determined by extraction with dithionite-citrate-bicarbonate (Mehra and Jackson 1960) following destruction of organic matter using pH 9.5, 5.25% NaOCl (Anderson 1963).
- Sand content was determined by wet and dry sieving.
- Clay content was determined by the pipette method (Gee and Bauder 1986).
- Silt content was determined by difference.

Some of the CEC and free iron oxide values listed in Table 2-1 differ from those reported earlier (Amacher et al. 1986) because different horizons and batches of soil were used in the different studies and the CEC and DCB methods were changed or modified from those used earlier.

Metals

The 15 elements used and their forms and concentrations are listed in Table 2-2. Whenever possible, the nitrate salt of the cationic elements was used. Potassium, sodium, or ammonium salts of the oxyanion elements were used. Each solution contained a background salt of 0.005 M $\text{Ca}(\text{NO}_3)_2$.

Experimental procedure

Retention of the elements was studied using a batch equilibration method (Amacher et al. 1986). One-gram samples of each soil were mixed with 10-mL aliquots of the solutions. Replicate samples for each soil–element concentration combination were carried through the procedure. In addition, one sample for each concentration without soil was carried through the procedure to account for possible contamination or other sorption losses. The samples were shaken for 18 hr at 100 osc min^{-1} , filtered through quantitative filter paper, and analyzed by ICP (inductively coupled plasma) emission spectrometry.

The amount of each element retained by each soil s (mg kg^{-1}) was calculated from the initial concentration in solution (mg L^{-1}) and the final concentration c in solution (mg L^{-1}).

The parameters K_d and b in eq 2-1 were determined for each soil and element combination using nonlinear regression analysis (SAS 1985).

RETENTION CHARACTERISTICS

Because of a high degree of retention of certain elements by some of the soils, many of the final element concentrations were at or below the practical detection limit of the ICP instrument. Since these data points were not reliable, they had to be discarded. Of the original 3300 measurements, 1564 could be used. The detection limit for most of the elements was between 0.05 and 0.1 mg L^{-1} . It was lower for Cd and Co (0.01 to 0.02 mg L^{-1}), and higher for B and Se ($>0.5 \text{ mg L}^{-1}$). Because the original concentrations were higher, all P and S final concentrations were well above their detection limits.

Table 2-2. Concentrations and forms of elements.

Element	Form	Concentrations
Co	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	A
Ni	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	A
Cu	$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$	A
Zn	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	A
Cd	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	A
Hg	HgCl_2	B
V	NH_4VO_3	A
Cr	$\text{K}_2\text{Cr}_2\text{O}_7$	A
Mo	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	A
B	H_3BO_3	A
Pb	$\text{Pb}(\text{NO}_3)_2$	A
P	KH_2PO_4	D
As	$\text{Na}_3\text{HASO}_4 \cdot 7\text{H}_2\text{O}$	A
S	Na_2SO_4	C
Se	Na_2SeO_4	A

A: 0.01, 0.05, 0.1, 0.2, 0.5, 1, 5, 10, 50, 100 mg L^{-1} .

B: 0.1, 0.2, 0.5, 1, 5, 10, 50, 100 mg L^{-1} .

C: 1, 2, 5, 10, 25, 50, 75, 100, 150, 200 mg L^{-1} .

D: 10, 20, 40, 60, 80, 100, 200, 300, 400, 500 mg L^{-1} .

Table 2-3. Freundlich model parameters K_d and b for 11 soils and 15 elements.

Element	Initial species	Class of species	Soil*										Mean†	Coeff. of variation (%)	
			AL	CA	CE	KU	LA	MO	NO	OL	SP	WE			WI
log K															
Co	Co ²⁺	Cation	1.553	2.400	0.817	2.022	1.530	1.966	1.437	1.826	0.407	2.560	0.798	1.574 bcdefghik	43.2
Ni	Ni ²⁺	Cation	1.578	2.314	0.835	2.042	1.700	1.652	1.321	1.703	0.536	2.527	0.926	1.558 bcdefghijk	39.7
Cu	Cu ²⁺	Cation	2.411	3.419	1.730	3.311	2.345	2.566	1.950	2.338	1.750	3.803	1.887	2.501 ab	28.5
Zn	Zn ²⁺	Cation	1.448	2.623	1.049	2.376	1.303	1.905	1.624	1.950	0.326	2.889	0.986	1.680 bcdefgh	45.6
Cd	Cd ²⁺	Cation	1.720	2.460	1.142	2.271	1.722	1.960	1.459	1.991	0.738	2.878	1.157	1.773 bcdefg	35.6
Hg	Hg ²⁺	Cation	2.035	1.292	1.910	2.397	2.278	2.079	2.053	2.109	1.936	2.476	2.115	2.062 bc	15.1
Pb	Pb ²⁺	Cation	3.257	CS*	2.372	7.635	2.963	3.912	2.585	4.215	2.135	CS	2.674	3.528 a	47.8
V	VO ₃	Oxyanion	2.152	1.035	1.599	3.347	2.012	2.703	1.270	1.960	1.958	1.907	2.184	2.012 bcd	31.4
Cr	CrO ₄ ²⁻	Oxyanion	0.533	NS*	NS	1.798	1.482	0.807	NS	NS	0.738	NS	0.928	1.048 cdefghijkl	46.5
Mo	Mo ₇ O ₆ ³⁻	Oxyanion	1.760	NS	1.256	2.614	1.911	2.071	NS	NS	1.409	NS	1.641	1.809 bcdef	25.0
B	BO ₃ ³⁻	Oxyanion	0.172	-0.070	NS	0.925	NS	0.143	NS	NS	NS	0.204	NS	0.275 jkl	137.9
P	PO ₄ ³⁻	Oxyanion	1.543	1.115	1.547	2.889	2.174	2.239	NS	1.649	2.237	1.585	2.163	1.914 bcde	26.9
As	AsO ₄ ³⁻	Oxyanion	1.679	0.948	1.297	3.176	1.851	2.194	0.931	1.663	1.273	1.373	2.021	1.673 bcdefghi	38.5
S	SO ₄ ²⁻	Oxyanion	NS	NS	NS	0.909	NS	-0.378	NS	NS	NS	NS	NS	0.265	342.8
Se	SeO ₄ ²⁻	Oxyanion	NS	NS	NS	0.958	NS	NS	NS	NS	NS	NS	NS	0.958	—
b															
Co	Co ²⁺	Cation	0.953	0.546	0.745	0.878	1.009	0.621	0.627	0.584	0.811	0.782	0.741	0.754 bcde	20.1
Ni	Ni ²⁺	Cation	0.939	0.504	0.688	0.738	0.903	0.720	0.661	0.646	0.836	0.748	0.741	0.739 bcdef	16.5
Cu	Cu ²⁺	Cation	0.544	1.140	0.546	1.016	0.987	0.516	0.471	0.495	0.602	1.420	0.567	0.755 bcd	43.2
Zn	Zn ²⁺	Cation	1.011	0.510	0.724	0.724	0.891	0.675	0.515	0.625	0.962	0.697	0.792	0.739 bcdefg	22.3
Cd	Cd ²⁺	Cation	0.902	0.568	0.768	0.721	0.850	0.773	0.668	0.658	0.840	0.569	0.782	0.736 bcdefgh	15.1
Hg	Hg ²⁺	Cation	0.741	0.313	0.564	1.700	0.751	0.960	0.582	1.122	0.513	2.158	0.681	1.008 ab	52.3
Pb	Pb ²⁺	Cation	0.853	CS	0.662	5.385	0.558	1.678	0.741	0.998	0.743	CS	0.743	1.485 a	101.7
V	VO ₃	Oxyanion	0.592	0.857	0.629	1.402	0.679	0.847	0.877	0.607	0.483	0.762	0.647	0.762 bc	32.3
Cr	CrO ₄ ²⁻	Oxyanion	0.504	NS	NS	0.609	0.374	0.607	NS	NS	0.394	NS	0.521	0.501 bcdefghijkl	20.1
Mo	Mo ₇ O ₆ ³⁻	Oxyanion	0.882	NS	0.617	1.031	0.607	0.664	NS	NS	0.451	NS	0.544	0.685 abcdefghij	29.5
B	BO ₃ ³⁻	Oxyanion	0.363	0.787	NS	0.891	NS	0.518	NS	NS	NS	0.641	NS	0.626 abcdefghijk	30.4
P	PO ₄ ³⁻	Oxyanion	0.508	0.829	0.250	0.586	0.466	0.303	NS	0.321	0.247	0.506	0.293	0.431 bcdefghijkl	43.0
As	AsO ₄ ³⁻	Oxyanion	0.636	0.554	0.618	1.462	0.747	0.561	0.510	0.548	0.797	0.648	0.601	0.698 bcdefghi	38.3
S	SO ₄ ²⁻	Oxyanion	NS	NS	NS	0.811	NS	1.018	NS	NS	NS	NS	NS	0.914	16.0
Se	SeO ₄ ²⁻	Oxyanion	NS	NS	NS	0.986	NS	NS	NS	NS	NS	NS	NS	0.986	—

* Soils: AL: Aligator, CA: Calceitrid, CE: Cecil, KU: Kula, LA: Lafitte, MO: Molokai, NO: Norwood, OL: Olivier, SP: Spodosol, WE: Webster, WI: Windsor;

NS: no sorption, CS: complete sorption;

† Means not followed by the same letter are significantly different at the 0.05 probability level.

In complex heterogeneous systems consisting of many components, such as soils, many of the element retention reactions will not attain equilibrium in the 18-hr period used in this study. Only the more rapid surface exchange and complexation reactions will attain equilibrium in this time period (Amacher et al. 1988). Nevertheless, simple equilibrium models such as the Freundlich equation can still be used to describe retention data at a single point in time, and this is the approach used here.

For this study we considered only the total concentrations of the elements of interest even though it is clearly recognized that numerous hydrolysis and other species will form in solution and on the soil surfaces. To further complicate matters, elements such as V, Cr, Co, Hg, As, and Se can undergo redox reactions with soil components such as organic matter and manganese oxides. Thus, the initial form of the ions may change upon reaction with the soil, although the rates of these transformations are often quite slow (e.g., Cr[VI] reduction by organic matter at normal soil pH levels [Amacher and Baker 1982]). Different results should be expected if different element species are reacted with the soils. To simplify the discussion, we use the element symbols to refer to the initial ion species used (Table 2-2).

Usually the logarithmic form of the Freundlich equation is used rather than the exponential form, but linear regression using the logarithmic form may produce different parameters than nonlinear regression using the exponential form. We used the exponential form of the Freundlich equation and determined K_d and b by nonlinear regression analysis. Kinniburgh (1986) also recommended this approach.

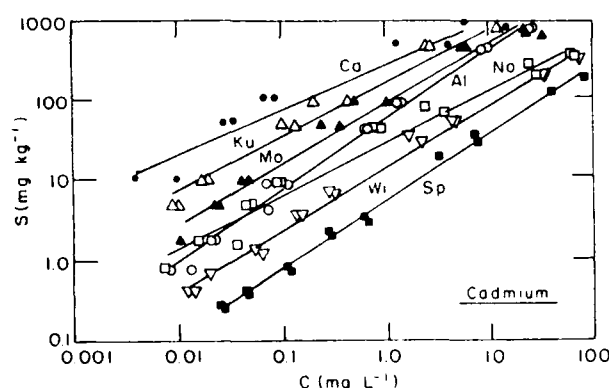


Figure 2-1. Retention isotherms for cadmium on selected soils. The soil abbreviations are defined in Table 2-3.

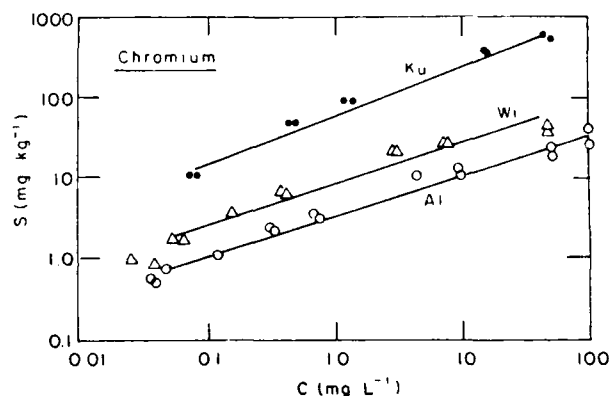


Figure 2-2. Retention isotherms for chromium on selected soils. The soil abbreviations are defined in Table 2-3.

Retention isotherms of a cation species (Cd) and an oxyanion species (Cr) for several soils are shown in Figures 2-1 and 2-2 as examples. Similar isotherms were obtained for other elements and soils. For a given solution concentration, soils with a high pH or CEC or that contained large amounts of iron and aluminum oxides retained more of a given cation species than did low-pH or low-CEC soils or soils with minor amounts of metal oxides. Soils with large amounts of metal oxides also retained more of a given oxyanion species than did those with minor amounts of metal oxides. Low-pH soils retained more of a given oxyanion species than high pH soils, which is in contrast to cation retention.

Retention isotherms for several cation and anion species on an Alligator soil are shown in Figures 2-3 and 2-4 for comparison. Similar isotherms were produced for the other soils. In general, Cu and Pb were strongly retained compared to the other cation species. Greater retention of V, Mo, P, and As as compared to Cr and B was observed.

For some element and soil combinations (figures not shown), deviations from the Freundlich isotherm were observed at low and high concentrations. Deviations at low concentrations are thought to be a result of analytical uncertainties in the data. Deviations at high concentrations are likely to be violations of the requirement that, for the Freundlich equation to be applicable, the solute species of interest be at low concentrations relative to the concentrations of other ions they are replacing on the soil surfaces (Sposito 1980).

Estimated values for $\log K_d$ and b are shown in Table 2-3. The SAS general linear model (GLM) and Tukey's mean separation method were used to determine if mean $\log K_d$ and b values for each element were significantly

Table 2-4. Simple correlation coefficients for selected soil properties and Freundlich parameters.

Soil property	Elements										
	Co	Ni	Cu	Zn	Cd	Hg	Pb	V	Cr	Mo	B
	Correlation coefficient (r) for log K_d										
pH	0.688*	0.622*	0.613*	0.788†	0.666*	ns	ns	ns	ns	ns	ns
TOC	ns	ns	ns	ns	ns	ns	NS	ns	ns	0.905*	ns
CEC	0.671*	0.755†	0.755†	0.608*	0.740†	ns	NS	ns	ns	ns	ns
OH	ns	ns	ns	ns	ns	ns	0.907†	ns	ns	0.804*	0.642*
MnO ₂	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Amorph. Fe ₂ O ₃	ns	ns	ns	ns	ns	ns	0.759*	0.689*	0.950†	0.809*	0.982†
Free Fe ₂ O ₃	ns	ns	ns	ns	ns	ns	ns	0.654*	ns	ns	0.814†
Al ₂ O ₃	ns	ns	ns	ns	ns	ns	0.908†	0.822†	ns	0.844*	0.610*
Sand	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	0.777†
Silt	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Clay	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	Correlation coefficient (r) for b										
pH	-0.742†	-0.845†	ns	-0.859†	-0.942†	ns	ns	ns	0.984**	ns	ns
TOC	0.724*	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
CEC	ns	ns	0.750†	ns	ns	0.722*	ns	ns	ns	ns	ns
OH	ns	ns	ns	ns	ns	ns	0.970†	0.876†	ns	ns	0.854†
MnO ₂	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Amorph. Fe ₂ O ₃	ns	ns	ns	ns	ns	ns	0.849†	0.637*	ns	ns	0.821†
Free Fe ₂ O ₃	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Al ₂ O ₃	ns	ns	ns	ns	ns	ns	0.973†	0.840†	ns	ns	0.915†
Sand	ns	ns	ns	ns	ns	ns	ns	ns	ns	0.956*	ns
Silt	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Clay	ns	ns	ns	ns	ns	ns	ns	ns	ns	-0.975†	ns

ns = not significant

* and † indicate significance at 0.05 and 0.01 probability levels, respectively.

Figure 2-3. Retention isotherms for selected cation species on Alligator soil.

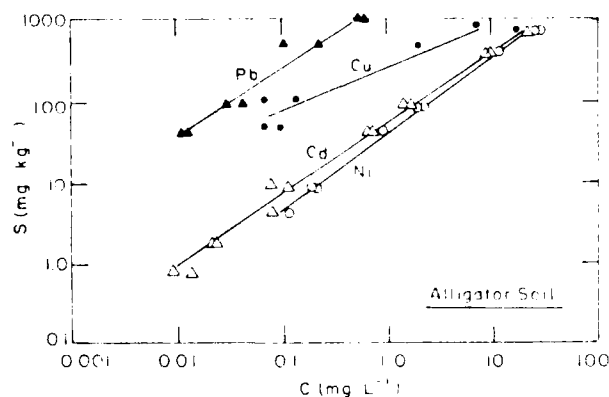
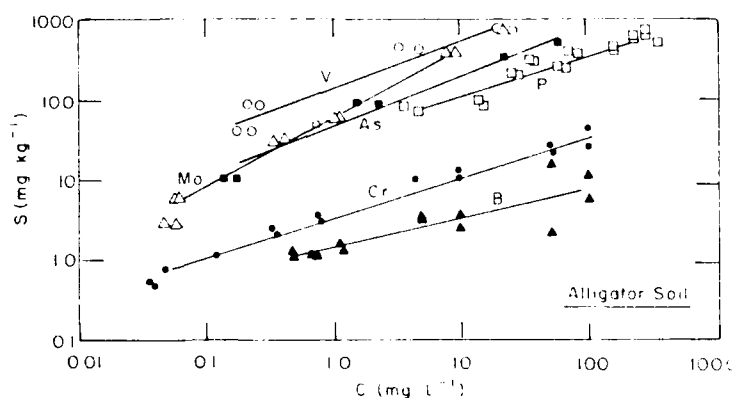


Figure 2-4. Retention isotherms for selected anion species on Alligator soil.



mean separation method were used to determine if mean $\log K_d$ and b values for each element were significantly different over soils (SAS 1985). The results are presented in Table 2-3. Strongly retained ions such as Pb, Hg, Cu, V, and P had the highest K_d values, as expected. Cationic species tended to have higher b values than the oxyanions overall. Phosphorus had the lowest b values observed. Among the cations, the strongly retained Pb, Hg, and Cu species had the highest b values (for some soils $b > 1$) and had the most variability in b values across soils. The oxyanions also had highly variable b values across soils.

A T-test was used to compare b pairwise (Steel and Torrie 1980 [p. 258]) for each soil and element combination; from Figure 2-5 it is possible to determine whether b for a given element-soil combination is significantly different from b for another element-soil combination. Match an element listed in the column on the left side of Figure 2-5 with another element listed in the row across the top. For each soil position in the square an x, a blank space, or a dot symbol is shown. An x indicates that the b values for the particular pair of elements being compared for an individual soil are not statistically different at the 0.05 level of probability. A blank space indicates that the b values being compared are statistically different. A dot indicates that one or both b values in the paired comparison are missing. The soils are arranged in each square alphabetically beginning in the upper left corner. The transition metal cations Co and Ni and the group IIB cations Zn and Cd tended to have the same b values for any given soil. Although Hg is a group IIB cation, b values for Hg were different from those for Zn and Cd in many cases largely because of stronger retention of Hg by the soils.

Among the transition metal cations, Cu had the highest and lowest b values and the highest K_d values. Among the transition elements, Cu also has the highest stability constants for divalent ion complexes of a given ligand in solution. Thus, if formation of complexes between Cu and soil surface binding sites is analogous to formation of solution complexes of Cu, and if K_d is analogous to stability constants for complexes, then the higher K_d values for Cu are in accord with this theory. Among the transition element oxyanions, Cr had lower K_d and b values than V and Mo for all soils. Among the main group oxyanions, B had lower K_d values than As or P, and b values for the three elements were highly soil-dependent.

We correlated the $\log K_d$ and b values to the soil properties listed in Table 2-1. The simple correlation coefficients for statistically significant relationships are listed in Table 2-4. The $\log K_d$ values for the transition

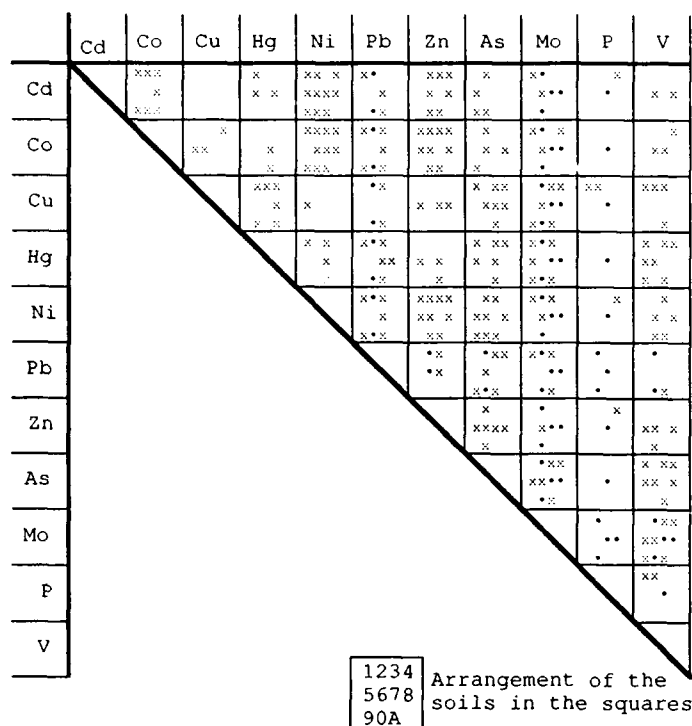


Figure 2-5. Comparison chart of soils and elements for Freundlich parameter b . The soils are represented by the following characters: Alligator (1), Calciorthid (2), Cecil (3), Kula (4), Lafitte (5), Molokai (6), Norwood (7), Olivier (8), Spodosol (9), Webster (0), Windsor (A). Statistically similar b parameters (0.05 level of probability) are represented by an \times ; missing values are represented with a \cdot .

K_d and pH is often observed for a given sorbing material (e.g., Kurbatov plots [Sposito 1984]). Since soils contain many different sorbing materials, K_d and pH relationships for a given soil or among soils as was observed in this study are a result of many complex interactions. Further work is needed on the nature of K_d and pH relationships for single sorbing materials, mixtures of materials, soils, and groups of soils. Quantitative relationships among single sorbents, soils, and groups of soils would have some predictive value in modeling studies.

Strong correlations between soil pH and b values for the transition metal cations and group IIB metals were also found, except for Cu and Hg. Although $\log K_d$ and b for the oxyanions were not statistically related to pH (except b for Cr), soil pH does control oxyanion retention (Sposito 1984, Hingston 1981). The oxyanions were not retained (Cr and Mo) or had lower $\log K_d$ values (V, B, P, As) for the high-pH Calciorthid, Norwood, and Webster soils. The strong negative correlation between soil pH and b for cation species and the strong positive correlation between soil pH and b for Cr suggested that regression equations relating b and soil pH could be developed. This was done (see Figure 2-6). These relationships can be used to estimate b values for soils where Co, Ni, Zn, Cd, or Cr retention data are not available, but the soil pH is known.

Retention parameters for Pb (both K_d and b) were strongly correlated to exchangeable OH, amorphous Fe_2O_3 , and Al_2O_3 contents. Retention parameters for the oxyanions were also related to exchangeable OH, amorphous Fe_2O_3 , and Al_2O_3 contents. This is expected, since retention of oxyanions in soils is generally due

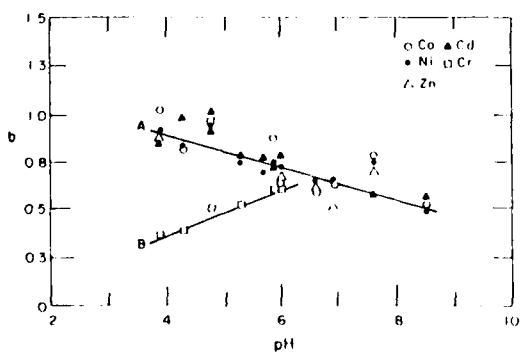


Figure 2-6. Correlation between soil pH and b values. Curve A is a regression line for Co, Ni, Zn, and Cd such that $b = 1.24 - 0.0831 \text{ pH}$ with a coefficient for correlation $r = 0.83$. Curve B is for Cr where $b = -0.0846 + 0.116 \text{ pH}$ with $r = 0.98$.

to binding by metal oxides (Sposito 1984). Significant correlations of $\log K_d$ to amorphous Fe_2O_3 content are more likely than correlations to free Fe_2O_3 content. Apparently the magnitude of K_d is somewhat sensitive to the amorphous iron oxide content of a soil. Thus, the amorphous iron oxide content of soils would appear to be a better indicator of anion retention than free iron oxide content. Sulfur was retained only by the Kula and Molokai soils, which contain higher amounts of metal oxides and amorphous material than the other soils, and Se (selenate form) was retained only by the Kula soil.

The results of these retention experiments lead to the following conclusions:

- 1) pH is the most important soil property that affects K_d and b .
- 2) CEC influences K_d for cation species.
- 3) The amounts of amorphous iron oxides, aluminum oxides, and amorphous material in soils influences both cation and anion retention parameters.
- 4) Except for Cu and Hg, transition metal (Co and Ni) and group IIB cations (Zn and Cd) have similar K_d and b values for a given soil.
- 5) Significant relationships between soil properties and retention parameters exist even in a group of soils with very different characteristics.

The relationships between soil properties and retention parameters (e.g., Fig. 2-6) can be used to estimate retention parameters when retention data for a particular element and soil type are lacking but soil property data are available. For example, the retention characteristics of Co, Ni, Zn, and Cd are sufficiently similar so that these elements can be grouped together, and an estimated b value for any one of them could be estimated from soil pH data using the regression equation for curve A in Figure 2-6. For many purposes such an estimate would be useful, at least as a first approximation, in describing the retention characteristics of a soil.

Chapter 3. A Kinetic Multireaction Approach

Retention reactions that occur in the soil are important processes that govern the fate of chemical contaminants such as heavy metals and organics in groundwaters. Mathematical models that describe the potential mobility of dissolved chemicals must, therefore, include the physical, chemical, and biological processes that influence their behavior in the soil matrix. The ability to predict the mobility of heavy metals in soil and the potential contamination of groundwater supplies has considerable health implications and is necessary for determining the degree of pollution, and for cleanup of former disposal sites.

In this study, two conceptual-type models (MRTM and MRM) were developed to describe the fate of heavy metals in soils. Both models are based on multiple retention reactions of the reversible and irreversible type. The retention mechanisms include nonlinear equilibrium as well as linear and nonlinear kinetic reactions. The MRTM deals with the transport and retention of heavy metals in soil with time and depth. The MRM describes batch or kinetic type retention where a no-water-flow condition is considered. Batch-type experiments are often carried out to quantify the mechanisms of the retention processes. The equations representing the two models were solved using numerical approximation methods. Sensitivity analysis of model results of retention and transport of heavy metals has been carried out for a wide range of reaction rate coefficients. Computer algorithms for both models are given along with illustrative examples of model output results.

FORMULATION OF MODELS

Multireaction model (MRM)

The success of single-reaction kinetic as well as equilibrium-kinetic two-site models leads us to believe that a more universal multireaction (multisite) model is plausible. Accordingly, we present the general-purpose multireaction model (MRM) illustrated in Figure 3-1. We assume that the solute in the soil environment is present in the soil solution (c) and in several phases representing heavy metal retained by the soil (s_e, s_1, s_2, s_3 , and s_{irr}), where c and s are expressed in mg L^{-1} and mg kg^{-1} , respectively. In addition, we propose that the retention-release processes are governed by several concurrent as well as consecutive type reactions.

The sorbed phase s_e is considered as the amount of heavy metal that is sorbed reversibly and is in local equilibrium with that in soil solution phase (c) at all times (Figure 3-1). Therefore, we assume that the local equilibrium assumption between c and s_e is valid (Rubin 1983). The governing equilibrium reaction mechanism is that of the Freundlich equation (Helfferich 1962),

$$s_e = K_d c^b, \quad (3-1)$$

where K_d is the associated distribution coefficient and b is a Freundlich parameter. The value of parameter b based on batch studies was found to be consistently less than unity for several elements (Buchter et al. 1989).

The heavy metal present in the soil solution phase (c) is assumed to react kinetically (i.e., it is time dependent) and reversibly with s_1 , very slowly and reversibly with s_2 , and irreversibly with s_{irr} . The kinetic reaction between C and s_1 can be represented by (van Genuchten et al. 1974, Amacher et al. 1988)

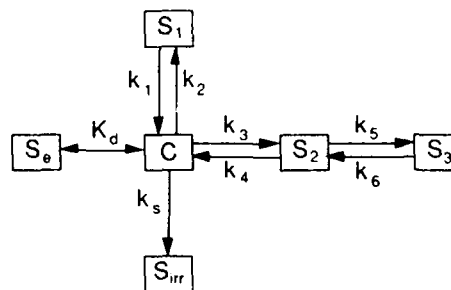


Figure 3-1. Schematic diagram of the multireaction retention model.

$$\rho (\partial s_1 / \partial t) = \Theta k_1 c^n - \rho k_2 s_1 \quad (3-2)$$

where k_1 and k_2 are the forward and reverse rate coefficients (hr^{-1}), ρ is the soil bulk density (g cm^{-3}) and Θ is the water content ($\text{cm}^3 \text{cm}^{-3}$). Parameter n (dimensionless) is the reaction order, where for $n \neq 1$, the reaction is nonlinear. Since it is assumed that c and s_1 react rapidly and reversibly, k_1 and k_2 are considered relatively large in magnitude. If c and s_1 reach equilibrium almost instantaneously, the ratio k_1/k_2 is the equilibrium constant for that reaction.

The kinetic reaction between c and s_2 may be represented by

$$\rho (\partial s_2 / \partial t) = \Theta k_3 c^m - \rho k_4 s_2 \quad (3-3)$$

where k_3 and k_4 (hr^{-1}) are the forward and reverse rate coefficients, respectively, and m is the reaction order. Eq 3-3 is similar to eq 3-2, except that reaction 3-3 is considered to be more kinetic than reaction 3-2. As a result the magnitudes of rate coefficients k_3 and k_4 are smaller than k_1 and k_2 in eq 3-2. Moreover, the reaction was considered to be nonlinear, where $m \neq 1$ and m and n need not be the same.

The reaction between c and s_{irr} may be represented by

$$\rho (\partial s_{\text{irr}} / \partial t) = \Theta k_s c \quad (3-4)$$

where k_s is the rate coefficient for the irreversible retention reaction. Thus, s_{irr} represents an irreversible sink term.

An extension of the concurrent multireaction model includes a consecutive reaction (Figure 3-1). The concurrent-consecutive multireaction model includes an additional retention phase, s_3 . This phase represents the amount of solute strongly retained by the soil that reacts slowly and reversibly with s_2 . Thus, inclusion of s_3 in the model allows the description of the frequently observed very slow release of solute from the soil (Selim 1981). The reaction between s_2 and s_3 was considered to be of the kinetic first-order type, i.e.

$$(\partial s_3 / \partial t) = k_5 s_2 - k_6 s_3 \quad (3-5)$$

where k_5 and k_6 (hr^{-1}) are the reaction rate coefficients. If a consecutive reaction is included in the model, then eq 3-3 must be modified to incorporate the reversible reaction between s_2 and s_3 . As a result, the following equation

$$\rho (\partial s_2 / \partial t) = \Theta k_3 c^m - \rho k_4 s_2 - \rho k_5 s_2 + \rho k_6 s_3 \quad (3-6)$$

must be used in place of eq 3-3.

The MRM is necessary for the description of kinetic and/or equilibrium retention behavior of sorption-desorption isotherms for heavy metals in soils. Isotherms that represent the amount sorbed or retained by the soil vs the amount in soil solution are often obtained using batch-type experiments for a range of initial (or applied) solute concentrations and for a given soil-to-solution ratio. For most isotherms, the time of contact often ranges from a few hours (4 to 8) or commonly 1 day of reaction time. However, for heavy metals that interact slowly, a set of isotherms with each representing one reaction time is often obtained. The MRM is capable of describing such isotherms for a given initial concentration with time as desired. For additional details on kinetic heavy metal isotherms, refer to Amacher et al. (1986, 1988).

Multireaction and transport model (MRTM)

This model represents an extension of the multireaction model (MRM) to include transport in addition to retention behavior of heavy metals in the soil environment. To describe the mobility of heavy metals in the soil profile, the classic convective-dispersive transport equation was used. For one-dimensional, steady-state water flow conditions, the transport equation for reactive solutes may be expressed as (Brenner 1962, Nielsen et al. 1986)

$$\rho \partial s / \partial t + \Theta \partial c / \partial t = \Theta D \partial^2 c / \partial x^2 - v \partial c / \partial x - Q \quad (3-7)$$

where c is solute concentration in solution (mg L^{-1}), Θ is the soil water content ($\text{cm}^3 \text{cm}^{-3}$), ρ is the soil bulk density (mg cm^{-3}), D is the hydrodynamic dispersion coefficient ($\text{cm}^2 \text{hr}^{-1}$), v is Darcy's water flux density (cm hr^{-1}), x is soil depth (cm), and t is time (hr). In addition, s is the solute concentration associated with the solid phase of the soil ($\text{mg kg}^{-1} \text{soil}$), and Q is the rate of solute removal (or supply) from soil solution ($\text{mg cm}^{-3} \text{hr}^{-1}$) and is not included in s .

In a fashion similar to the multireaction model discussed by Amacher et al. (1988), we consider the $\partial s / \partial t$ term to describe fully reversible processes between the solution and the solid phases. Specifically, we consider the reversible retention to be of the multireaction (multisite) equilibrium-kinetic type where s is composed of four phases:

$$s = s_e + s_1 + s_2 + s_3 \quad (3-8)$$

Here we assume s_e as the amount of solute metal ($\text{mg kg}^{-1} \text{soil}$) that is sorbed reversibly and is in equilibrium with that in soil solution phase (c) at all times. The governing equilibrium retention-release mechanism is that of the nonlinear Freundlich type as described previously in the MRM,

$$s_e = K_d c^b \quad (3-9)$$

where K_d is the associated distribution coefficient ($\text{cm}^3 \text{kg}^{-1}$), and b is a dimensionless Freundlich parameter ($b < 1$).

The retention-release reactions associated with s_1 , s_2 , and s_3 are concurrent- or consecutive-type kinetic reactions (Figure 3-1). Specifically, the s_1 and s_2 phases were considered to be in direct contact with c , and reversible processes of the (nonlinear) kinetic type govern their reactions (Amacher et al. 1988, Selim et al. 1989):

$$\partial s_1 / \partial t = k_1 (\Theta / \rho) c^n - k_2 s_1 \quad (3-10)$$

$$\partial s_2 / \partial t = k_3 (\Theta / \rho) c^m - k_4 s_2 - k_5 s_2 + k_6 s_3 \quad (3-11)$$

$$\partial s_3 / \partial t = k_5 s_2 - k_6 s_3 \quad (3-12)$$

where k_1 and k_2 are the forward and backward rate coefficients (hr^{-1}), respectively, and n is the reaction order associated with s_1 . Similarly, k_3 , k_4 , and m are the reaction parameters associated with s_2 , and k_5 and k_6 are the reaction parameters associated with s_3 . These sorbed phases may be regarded as the amounts sorbed on surfaces of soil particles and chemically bound to aluminum and iron oxide surfaces or other types of surfaces, although it is not necessary to have a priori knowledge of the exact retention mechanisms for these reactions to be applicable. Moreover, these phases may be characterized by their kinetic sorption and release behavior to the soil solution and thus are susceptible to leaching in the soil. In addition, the primary difference between these two phases lies not only in the difference in their kinetic behavior but also in the degree of nonlinearity as indicated by parameters n and m .

The sink-source term Q of eq 3-7 is commonly used to account for irreversible reactions such as precipitation-dissolution, mineralization, and immobilization. We expressed the sink term as a first-order kinetic process:

$$Q = \rho \partial s_s / \partial t = \Theta k_s C \quad (3-13)$$

where k_s is the associated rate coefficient (hr^{-1}). This sink term was expressed in terms of a first-order irreversible reaction for reductive sorption or precipitation or internal diffusion as described by Amacher et al. (1986, 1988). Eq 3-13 is similar to that for a diffusion-controlled precipitation reaction if one assumes that the equilibrium concentration for precipitation is negligible (Stumm and Morgan 1971).

The retention-release reactions of eq 3-10 through 3-13 include equilibrium and kinetic processes. The multireaction model developed by Amacher et al. (1988), on which this transport and retention process is based, is a fully kinetic one where local equilibrium with the solution phase was not implicitly considered. As will be discussed in subsequent sections, we found it essential in this study to incorporate a Freundlich-type equilibrium reaction (eq 3-9) into the transport model to predict the transport behavior using several miscible displacement

data sets. This will be described in a subsequent section. In the two-site model proposed by Selim et al. (1976) and Cameron and Klute (1977), a linear or nonlinear kinetic reaction and an equilibrium reaction were incorporated with the convection–dispersion transport equation 3-7.

Initial and boundary conditions

The retention reactions associated with the MRM seek to provide a solution for solute concentration in soil solution and sorbed phases as a function of time. To solve the MRM, the appropriate initial conditions must be specified (Selim et al. 1976, Selim 1978). The initial conditions were that of a given initial solute concentration in solution and assumed no solute retention at time zero, as is the case for batch kinetic experiments. Specifically, the necessary conditions are as follows:

$$c = C_i, \quad t = 0, \quad (3-14)$$

$$c = C_o, \quad t > 0, \quad (3-15)$$

$$s_e = s_1 = s_2 = s_3 = 0, \quad t = 0, \quad (3-16)$$

where C_i and C_o are the initial and applied (input) solute concentrations, respectively. The model can incorporate other conditions if the concentration for each sorbed solute species (s_e , s_1 , s_2 , and s_3) is different from zero at the initial time for simulation ($t = 0$). These values must be specified by the user, however.

To solve the transport and retention–release equations associated with the MRTM, the appropriate initial and boundary conditions must be specified. Here we restrict our analysis to steady-state water flow conditions in a homogeneous soil with uniform moisture distribution. Therefore, water flux v and soil moisture content Q are considered time-invariant. It is also assumed that a solute solution of known concentration (C_o) was applied at the soil surface for a given duration t_p and was thereafter followed by a solute-free solution. The conditions associated with such a pulse are frequently expressed as (Selim and Mansell 1976, van Genuchten and Parker 1984)

$$c = C_i, \quad t = 0, 0 < x < L \quad (3-17)$$

$$s_e = s_1 = s_2 = s_3 = 0, \quad t = 0, 0 < x < L \quad (3-18)$$

$$v C_o = -\Theta D \partial c / \partial x + v c, \quad x = 0, t < t_p \quad (3-19)$$

$$0 = -\Theta D \partial c / \partial x + v c, \quad x = 0, t > t_p \quad (3-20)$$

$$\partial c / \partial x = 0, \quad x = L, t > 0. \quad (3-21)$$

Equations 3-17 and 3-18 represent initial conditions for a soil profile of length L (cm) with uniform initial concentration C_i in the solution and devoid of sorbed phases along the soil profile at time zero. However, this model is not restricted to uniform conditions; rather, nonuniform initial distributions of c , s_e , s_1 , s_2 , and s_3 can be incorporated; they must be supplied by the user. Equations 3-19 and 3-20 represent a third type of boundary condition of solute convection and dispersion at the soil surface, where C_o is the applied solute concentration. These conditions simulate a solute pulse-type input for a duration t_p (hr) that is preceded and followed by a solute-free solution. Equation 3-22 represents a flux- or Newman-type boundary condition at the bottom ($x = L$) of the soil profile at all times t . For a discussion of boundary conditions that describe solute transport problems, see Selim and Mansell (1976).

The convection–dispersion solute transport eq 3-7 subject to the initial and boundary conditions described above was solved using finite-difference explicit-implicit methods (Remson et al. 1971, Pinder and Gray 1977). Finite-difference solutions provide distributions of solution and sorbed phase concentrations at incremental distances Δx and time steps Δt as desired. In a finite difference form a variable such as c is expressed as

$$c(x,t) = c(i \Delta x, j \Delta t) \quad (3-22)$$

$$\begin{aligned} \text{where } i &= 1, 2, 3, \dots, N & \text{and } j &= 1, 2, 3, \dots \\ x &= i \Delta x, & \text{and } t &= j \Delta t. \end{aligned} \quad (3-23)$$

For simplicity, the concentration $c(x, t)$ may be abbreviated as

$$c(x, t) = C_{i,j} \quad (3-24)$$

where subscript i denotes incremental distance in the soil and j denotes the time step. We assume that the concentration distribution at all incremental distances (Δx) is known for time j . We now seek to obtain a numerical approximation of the concentration distribution at time $j+1$. The convection-dispersion eq 3-7 must be expressed in a finite difference form. For the dispersion and convection terms, the finite difference forms used are

$$\begin{aligned} \Theta D \partial^2 c / \partial x^2 &= \Theta D (C_{i+1,j+1} - 2 C_{i,j+1} + C_{i-1,j+1}) / 2(\Delta x)^2 \\ &+ \Theta D (C_{i+1,j} - 2 C_{i,j} + C_{i-1,j}) / 2(\Delta x)^2 + O(\Delta x)^2 \end{aligned} \quad (3-25)$$

and

$$v \partial c / \partial x = v (C_{i+1,j+1} - C_{i,j+1}) / \Delta x + O(\Delta x) \quad (3-26)$$

where $O(\Delta x)$ and $O(\Delta x)^2$ are the error terms associated with the above finite-difference approximations, respectively. In the above derivations, the second-order derivative (the dispersion term) is expressed in an explicit-implicit form commonly known as the Crank-Nickolson or central approximation method (Carnahan et al. 1969). This is obtained using Taylor series expansion and is divided equally for time j (known) and time $j+1$ (unknown). Such an approximation has a truncation error, as obtained from the Taylor series expansion, in the order of $(\Delta x)^2$, which is expressed here as $O(\Delta x)^2$. Moreover, in the above approximations, the convection term was expressed in a fully implicit form, which resulted in a truncation error of $O(\Delta x)$. In our numerical solution, for small values of Δx and Δt , these truncation errors were assumed to be sufficiently small and were therefore ignored (Henrici 1962).

The time-dependent term of eq 3-7 was expressed as

$$R \partial c / \partial t = R_{i,j} (C_{i,j+1} - C_{i,j}) / \Delta t + O(\Delta t) \quad (3-27)$$

where the retardation term R was solved explicitly as

$$R = 1 + (b \rho K_d / \Theta) c^{b-1}. \quad (3-28)$$

This was incorporated in a finite difference form using an iteration method due to the nonlinearity of the equilibrium (and kinetic) retention reactions. Specifically, the retardation term was expressed as

$$R = (R_{i,j})_r = 1 + (b \rho K_d / \Theta) (Y^{b-1})_r \quad (3-29)$$

where Y represents the average concentration over time step j (known) and that at time step $j+1$ for which solution is being sought, such that

$$Y_r = (C_{i,j+1} + C_{i,j}) / 2 \quad (3-30)$$

where r refers to the iteration steps.

For the kinetic retention equations, the time derivative for s_1 , s_2 , and s_3 were expressed in their finite-difference forms in a similar manner to the above equations. Therefore, omitting the error terms and incorporating the iteration scheme we have

incorporating the iteration scheme we have

$$\begin{aligned} \rho \partial s_1 / \partial t &= k_1 \Theta c'' - k_2 \rho s_1 \\ &= k_1 \Theta \{[(C_{i,j+1})_r + C_{i,j}]/2\}'' - k_2 \rho [(s_1)_{i,j}]_r \end{aligned} \quad (3-31)$$

$$\rho \partial s_2 / \partial t = k_3 \Theta \{[(C_{i,j+1})_r + C_{i,j}]/2\}''' - k_4 \rho [(s_2)_{i,j}]_r \quad (3-32)$$

$$\partial s_3 / \partial t = k_5 [(s_2)_{i,j}]_r + k_6 \rho [(s_3)_{i,j}]_r \quad (3-33)$$

Moreover, the irreversible term Q was expressed in an implicit-explicit fashion as

$$Q = k_s Q (C_{i,j+1} + C_{i,j})/2. \quad (3-34)$$

For each time step $(j+1)$, after rearrangement and incorporation of the initial and boundary conditions in their finite difference form, the finite difference of the solute transport equation can be represented by a set of N equations having N unknown concentrations. The form of the N equations is

$$a_{i,j} C_{i-1,j+1} + b_{i,j} C_{i,j+1} + u_{i,j} C_{i+1,j+1} = c_{i,j} \quad (3-35)$$

where N is the number of incremental distances in the soil ($N = L/\Delta x$). The coefficients a , b , u , and c are the associated set of equation parameters. The above N equations were solved simultaneously for each time step using the Gaussian elimination method (Carnahan et al. 1969) to obtain concentration C at all nodal points (i) along the soil profile. Specifically, subroutine TRIDM of the MRTM provides a solution for a set of linear equations using the Thomas algorithm for tridiagonal matrix-vector equations (Pinder and Gray 1977). The newly calculated C values were used as input parameters in the solution for the retention eq 3-31 through 3-34. The solution of these equations provides the amount of sorbed phases due to the irreversible and reversible reactions at the same time $(j+1)$ and incremental distances along the soil profile.

The numerical approximation scheme given above for the MRTM was also used in solving the solute retention equations associated with the MRM. The major exception here was in the way the sorbed phase concentration (s_e) was calculated. The approach used is based on the assumption that, for any given time step j , the amount in soil solution c and in the sorbed phase s_e are in local equilibrium (Rubin 1983) and their amounts are related by the K_d value according to the nonlinear Freundlich eq 3-1. Therefore, for any given time step, the total amount in the solution and sorbed phases is

$$H = \Theta c + \rho s_e \quad (3-36)$$

or

$$H = \Theta c + \rho K_d c^b \quad (3-37)$$

As a result, in the calculation procedure, from c and s_e the amount H was calculated for time step j . To estimate these variables at time step $j+1$ following the calculations of all other variables (i.e., s_1 , s_2 , etc.), we calculate a new value for H and partition such a value between c and s_e (based on the Freundlich equation) using the following implicit equation:

$$c = H/(\Theta + \rho K_d c^{b-1}), \quad (3-38)$$

which is derived directly from eq 3-37 and is based on the newly calculated for the sum of concentration and equilibrium sorbed phases, H . Equation 3-38 is an implicit equation for c and where iteration was necessary. Specifically, a solution for concentration C or specifically $C_{i,j}$ at each time step was obtained as follows:

$$C_r = H/(\Theta + \rho K_d [C^{b-1}]_{r-1}) \quad (3-39)$$

For the MRTM and MRM, the above equations must be solved in a sequential manner for each time step, until the desired time for simulation is attained. It should be emphasized that the number of iterations for the above calculations must be provided by the user. No criteria are given here for optimum number of iterations, rather a mass balance was performed (input vs output) as a check on the accuracy of the numerical solution. The user is free to adjust the number of iterations based on mass balance calculations or other criteria as desired. It is recommended that the number of iterations r be specified in the program such that 3–5% mass balance error is not exceeded.

SENSITIVITY ANALYSIS

To illustrate the kinetic behavior of heavy metal retention as governed by the multireaction and transport model (MRTM), several simulations were carried out. Figures 3-2 through 3-11 are selected simulations that illustrate the sensitivity of solution concentration results to a wide range of model parameters necessary for the MRTM with emphasis on the governing retention mechanism. The parameters selected for the sensitivity analyses were $\rho = 1.25 \text{ g cm}^{-3}$, $\Theta = 0.4 \text{ cm}^3 \text{ cm}^{-3}$, $L = 10 \text{ cm}$, $C_i = 0$, $C_o = 10 \text{ mg L}^{-1}$, and $D = 1.0 \text{ cm}^2 \text{ hr}^{-1}$. Here we

assumed a solute pulse was applied to a fully water-saturated soil column initially devoid of solute. In addition, a steady water-flow velocity (v) was maintained constant with a Peclet number $P (= vL/\Theta D)$ of 25. The length of the pulse was assumed to be 3 pore volumes, which was then followed by several pore volumes of a solute-free solution.

The influence of the distribution coefficient K_d , which is associated with s_e of the equilibrium-type reaction, on the transport of dissolved chemicals such as heavy metals is shown in Figure 3-2. Here the nonlinear parameter b was chosen as 0.5 and all reaction coefficients (k_1, \dots, k_6 , and k_s) were set equal to zero. As a result, the shape of the breakthrough curves (BTCs) of Figure 3-2 reflects the influence of a nonlinear Freundlich-type sorption of the equilibrium type. A BTC is a representation of solute concentration in the effluent solution expressed in terms of relative concentration (C/C_o) vs pore volume (V/V_o) of effluent, where C_o is the maximum or input concentration ($C_o = C_s$) and V_o is the pore volume ($V_o = \Theta L$).

For the nonreactive case ($K_d = 0$), which indicates no solute retardation, simulation results in Figure 3-2 indicate that the sorption (or effluent) side and the desorption side of the BTC are symmetrical. Here the solute concentration (C/C_o) slightly exceeds 0.5 for V/V_o of 1. As K_d increased, the solute became more retarded, as is clearly illustrated by the location of the sorption side of the BTCs. For example, for the case where $K_d = 2$, approximately three pore volumes were required before detection of solute in the effluent solution. In the meantime, a reduction of concentration maxima and the presence of tailing of the desorption side was observed for large K_d values. This is due not only to the large K_d values used but also to the nonlinearity of the equilibrium mechanism ($b \neq 1$) chosen here. In fact, the influence of a wide range of b values on the shape of the BTC is shown in Figures 3-3 and 3-4. For all the BTCs shown in Figures 3-3 and 3-4, a K_d of unity was used, with all other rate coefficients set equal to zero. For values of $b < 1$, the shape of the BTCs indicates a sharp rise in concentration or a steep sorption side with an increase of the tailing of the desorption side for decreasing values of b . In contrast, for $b > 1$ the sorption side indicates a slow increase of concentration, which is associated with a lack of tailing of the desorption side of the BTCs.

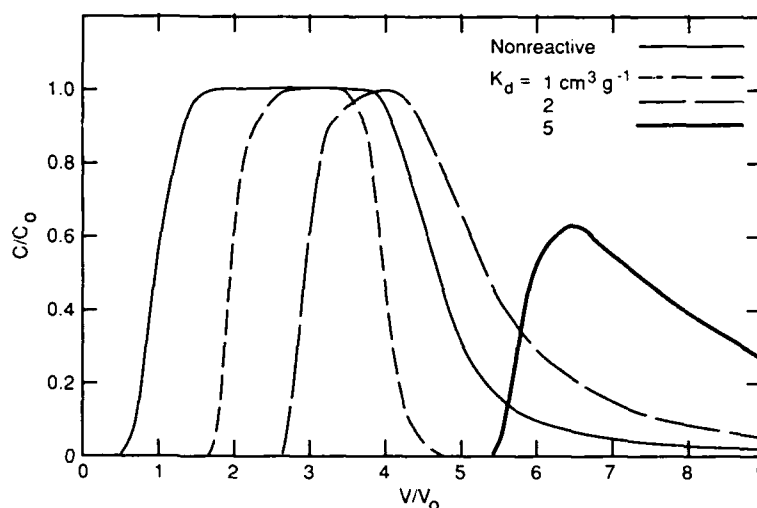


Figure 3-2. Breakthrough curves for several K_d values where $b = 0.5$ and $k_1 = k_2 = \dots = k_s = 0$.

Figure 3-3. Breakthrough curves for several b values where $b \leq 1.0$ and $k_1 = k_2 = \dots = k_s = 0$.

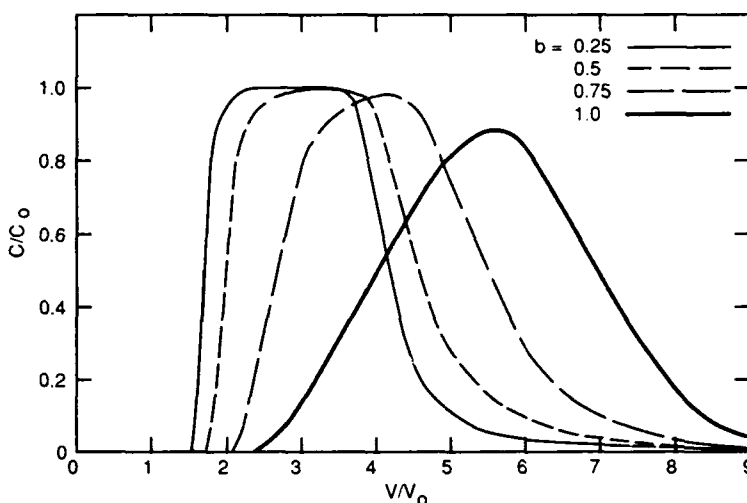
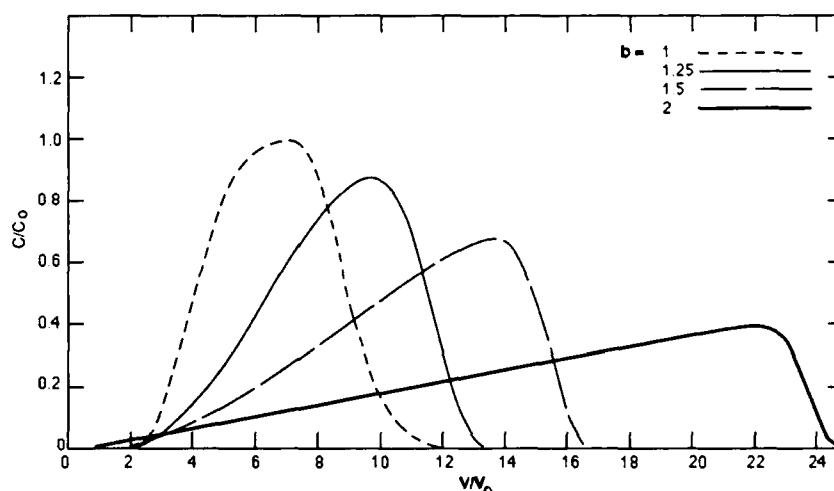


Figure 3-4. Breakthrough curves for several b values where $b \geq 1.0$ and $k_1 = k_2 = \dots = k_s = 0$.



The significance of rate coefficients k_1 and k_2 of the MRTM on solute retention and transport may be illustrated by the BTCs of Figures 3-5 and 3-6, where a range of rate coefficients differing by three orders of magnitude were chosen. For these simulations, values for k_3 to k_6 and k_s were maintained equal to zero and the equilibrium reaction was assumed linear where $K_d = 1 \text{ cm}^3 \text{ g}^{-3}$ and b was set equal to unity. For the BTCs shown in Figure 3-5, the forward rate coefficient was constant ($k_1 = 0.10 \text{ hr}^{-1}$) but k_2 varied from 1 to 0.001 hr^{-1} . A decrease in concentration maxima and a shift of the BTCs resulted as the value for k_2 decreased. Such a shift of the BTCs signifies an increase in solute retention due to the influence of the kinetic mechanism associated with s_1 . As the rate of backward reaction (k_2) decreases or k_1/k_2 increases, the amount of s_1 retained increases and solute mobility in the soil becomes more retarded. The BTCs of Figure 3-6 illustrate the significance of the magnitude of the kinetic rate reactions k_1 and k_2 while the ratio k_1/k_2 remains constant. It is obvious that as the magnitude of the rate coefficients increased, the amount of solute retained increased, and increased solute retardation became evident. Moreover, for extremely small k_1 and k_2 values (e.g., 0.001 hr^{-1}), the BTC resembles that for a nonreactive solute due to limited contact time for solute retention by the soil matrix under the prevailing water-flow velocity conditions. On the other hand, large rate coefficients are indications of fast or instantaneous retention reactions. Specifically, rapid reactions indicate that the retention process is less kinetic and approaches equilibrium conditions in a relatively short contact time.

Figure 3-7 shows BTCs for several values of nonlinear parameter n , which is associated with the kinetic retention reaction for s_1 . The BTCs of the previous figures and the simulations illustrated here have similar features. An increase in the value of n resulted in a decrease in peak solute concentration, which was accompanied by excessive tailing of the BTCs. No apparent shift of the BTCs shown was observed as n increased from 0.5

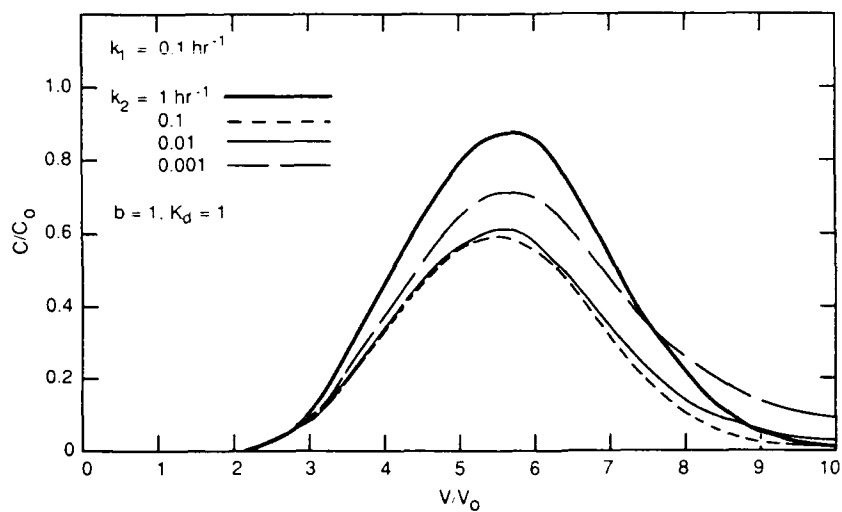


Figure 3-5. Breakthrough curves for several values of rate coefficients k_1 and k_2 (where $k_3 = k_4 = \dots = k_s = 0$).

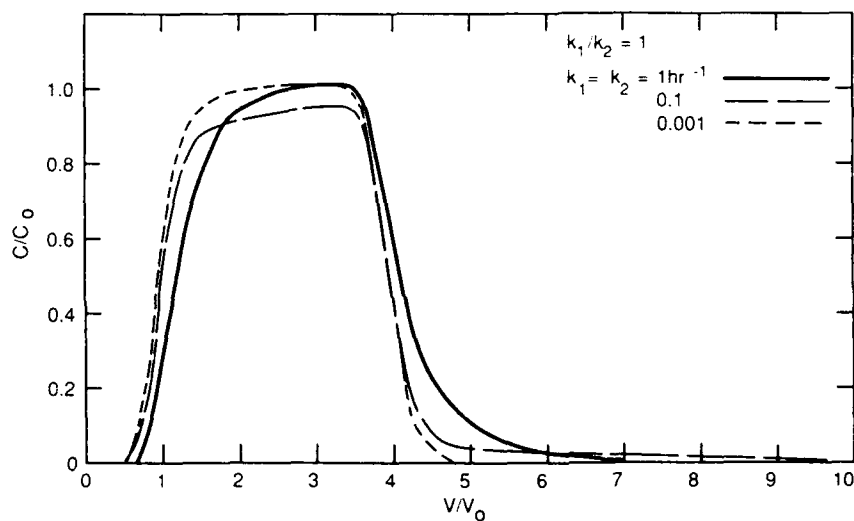


Figure 3-6. Breakthrough curves for several b values where k_1 and k_2 and k_1/k_2 remain invariant and $k_3 = k_4 = \dots = k_s = 0$.

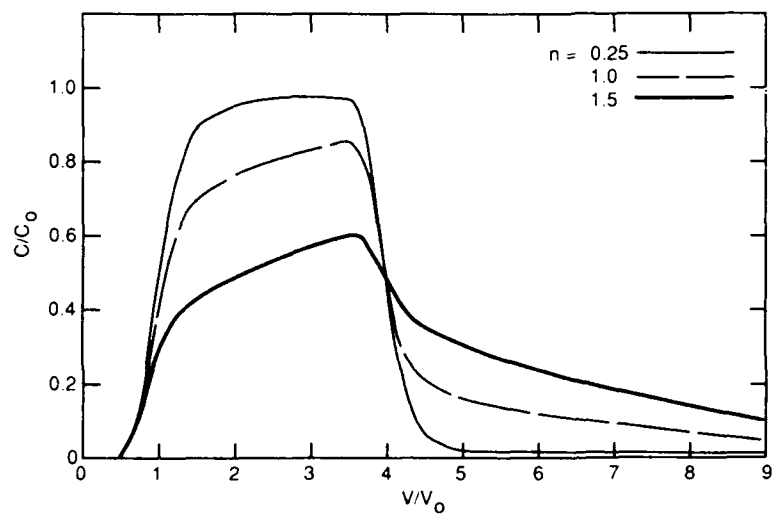


Figure 3-7. Breakthrough curves for several values of nonlinear parameter n associated with s_1 (where $k_3 = k_4 = \dots = k_s = 0$).

Figure 3-8. Breakthrough curves for several values of irreversible rate coefficient k_s (where $b = 1$ and $k_3 = k_4 = \dots = k_s = 0$).

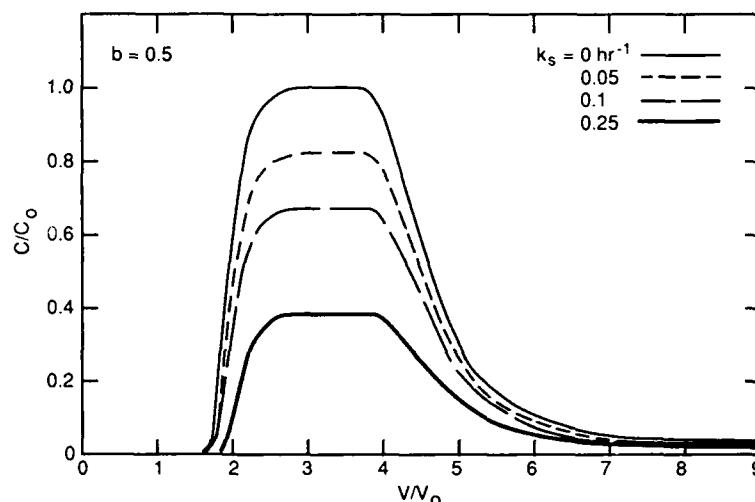
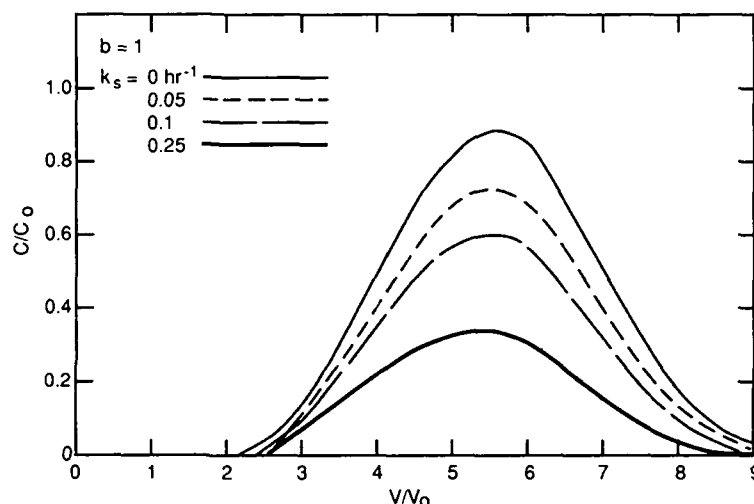


Figure 3-9. Breakthrough curves for several values of irreversible rate coefficient k_s (where $b = 0.5$ and $k_3 = k_4 = \dots = k_s = 0$).



to 1.5. Similarities between the influence of n and nonlinear parameter b associated with the equilibrium reactions are apparent when the BTCs shown in Figure 3-7 are compared with those of Figures 3-3 and 3-4.

In the BTCs in Figures 3-2 through 3-7, the irreversible retention mechanism for solute removal via the sink term was ignored (i.e., $Q = 0$). The influence of irreversible kinetic reaction is straightforward, as shown in Figures 3-8 and 3-9. This is manifested by the lowering of the solute concentration for the overall BTC for increasing values of k_s . Since a first-order irreversible reaction was assumed for the sink term, the amount of irreversibly retained solute (and thus the lowering of the BTC) is proportional to the solution concentration. The primary difference between the BTCs in Figures 3-8 and 3-9 is due to the value of nonlinear parameter n associated with the equilibrium retention mechanism. For the BTCs shown in Figure 3-8, $b = 0.5$, whereas a value of $b = 1$ was used for the BTCs shown in Figure 3-9. All other parameters remained constant: $k_1 = 0.001$, $k_2 = 0.01$ hr^{-1} , $K_d = 1$ cm^3 g^{-1} , and $k_3 = k_4 = k_5 = k_6 = 0$.

The presence of a consecutive-type reaction between s_2 and s_3 in the MRTM is manifested by the BTCs shown in Figures 3-10 and 3-11. In Figure 3-10, the influence of the magnitude of the rate of reactions k_5 and k_6 or specifically the ratio (k_5/k_6) , is illustrated. As k_5/k_6 increases, little influence on the retardation of the BTCs was observed. However, a decrease in peak concentration and an overall lowering of solute concentration of the desorption side is apparent. The incorporation of the s_3 phase in the model has the distinct advantage that one can assume that such a consecutive-type reaction may be regarded as a slow mechanism with a slow rate of reaction. Furthermore, if the backward rate is exceedingly small ($k_6 = 0$), the consecutive reaction becomes an irreversible mechanism. As a result, in this model the presence of an irreversible reaction may not be limited

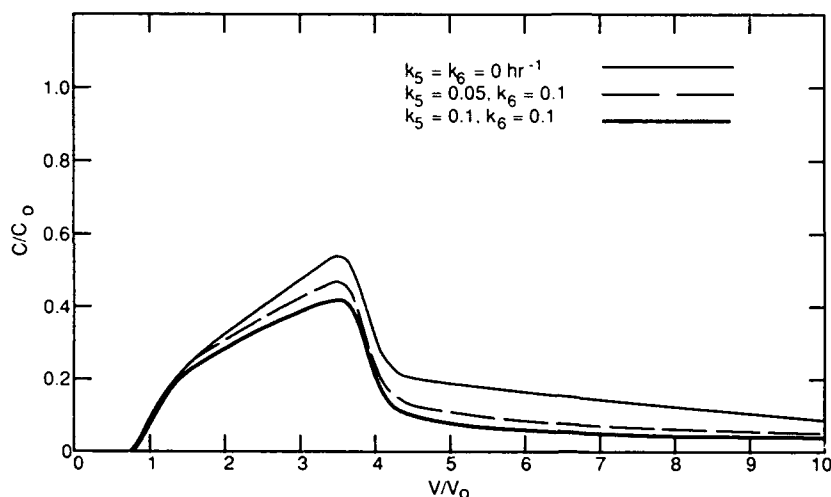


Figure 3-10. Breakthrough curves for several values of rate coefficients k_5 and k_6 (where $k_3 = k_4 = k_s = 0$).

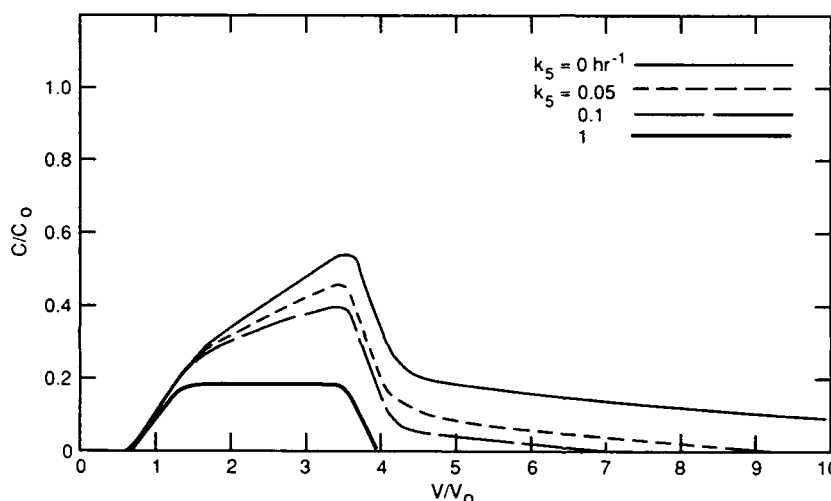


Figure 3-11. Breakthrough curves for several values of rate coefficient k_5 (where $k_3 = k_4 = k_6 = k_s = 0$).

of reaction. Furthermore, if the backward rate is exceedingly small ($k_6 = 0$), the consecutive reaction becomes an irreversible mechanism. As a result, in this model the presence of an irreversible reaction may not be limited to that of the sink term of eq 3-1 with a direct reaction with the soil solution. Simulations that illustrate the influence of irreversible retention for the consecutive reaction are shown in Figure 3-11.

MRM COMPUTER PROGRAM

The computer program for the MRM is written in the Fortran language. It consists of a source (or main) program only. The source program outlines the READ statements for the input parameters, the WRITE statements for the output data, and carries out all program calculations step by step in a sequential manner. The input and output variables used in the MRM are given in Tables 3-1 and 3-2, respectively. Since the MRM is an initial-value problem, no dependence on spatial dimension is present. As a result, there are no declared arrays of a given size in the computer code. Specifically, the DIMENSION statements that declare the size of variables in a given problem are not needed. This is an advantage in terms of the overall amount of memory that the program requires as well as in minimizing the need to modify the computer code. The user must familiarize himself with the computer code before making any modifications to it, and a Fortran compiler is required. Unless the user wishes to incorporate additional reactions or program his configuration, the computer code should not be changed.

A Fortran listing of the MRM computer code for use with personal computers is given in Appendix A. This

Table 3-1. List of input parameters required for MRM.

<i>Card number</i>	<i>Column number</i>	<i>Format</i>	<i>Variable name</i>	<i>Definition</i>
I	1-80	20A4	USER	User's name or any other information (optional)
II	1-80	20A4	SOIL	Soil name or any other information (optional)
III	1-80	20A4	SOLUTE	Solute species or other information (optional)
VI	1-80	20A4	DATE	Date, experiment number or other information (optional)
1	51-70	E20.6	TH	Soil moisture content (Θ), $\text{cm}^3 \text{cm}^{-3}$
2	51-70	E20.6	ROU	Soil bulk density (ρ), g cm^{-3}
3	51-70	E20.6	CS	Concentration of applied solute solution (C_0), mg L^{-1}
4	51-70	E20.6	KD	Distribution coefficient (K_d), $\text{cm}^3 \text{g}^{-1}$
5	51-70	E20.6	NEQ	Freundlich reaction order (b), dimensionless
6	51-70	E20.6	K1	Rate coefficient (k_1), hr^{-1}
7	51-70	E20.6	K2	Rate coefficient (k_2), hr^{-1}
8	51-70	E20.6	W	Order of reaction (n), dimensionless
9	51-70	E20.6	K3	Rate coefficient (k_3), hr^{-1}
10	51-70	E20.6	K4	Rate coefficient (k_4), hr^{-1}
11	51-70	E20.6	U	Order of reaction (m)
12	51-70	E20.6	KS	Irreversible rate coefficient (k_s), hr^{-1}
13	51-70	E20.6	K5	Rate coefficient (k_5), hr^{-1}
14	51-70	E20.6	K6	Rate coefficient (k_6), hr^{-1}
15	51-53	I3	IT	Number of iterations (r)
16	51-70	E20.6	TTOTAL	Total simulation time, hr
17	51-70	E20.6	TPRINT	Time interval for printout, hr
18	51-70	E20.6	DT	Initial guess for the time step (Δt), hr

Table 3- 2. List of output variables used in MRM.

<i>Variable</i>	<i>Definition</i>	<i>Units</i>
TIME	Simulation time (t)	hr
C	Solute concentration (c)	mg L^{-1}
TOTAL	Total amount of solute retained per unit weight (s)	mg kg^{-3}
S1	Amount of s_1	mg kg^{-1}
S2	Amount of s_2	mg kg^{-1}
S3	Amount of s_3	mg kg^{-1}
SIR	Amount of s_{irr}	mg kg^{-1}
SEQ	Amount of s_e	mg kg^{-1}
BAL	Mass balance of solute	%

sample input data file for use with the PC version is included in the appendix. We have provided a listing of the PC version of MRM rather than the mainframe version since they are essentially the same except for the input-output section. The PC version of MRM was compiled using a Fortran compiler for personal computers, and an executable file is also included.

To use this version of MRM, the user need only type MRMPc to run the program. You will then be prompted for the name and destination of an output file where all model calculations will be stored. If you choose to provide the input data interactively, you will also be prompted to enter the appropriate input parameters in the order given in the data file. For convenience, a range of values for soil parameters and reaction rate coefficients is also provided for each input to assist users unfamiliar with the MRM program and to provide a range of parameter values for sensitivity analysis for problems of interest. The ranges given here represent average values of soil properties and the rate coefficients; they were taken from Amacher et al. (1988).

If you make a mistake in entering an input value, we recommend that you terminate the program and run the model again by typing MRMPc.

A sample of output calculations using the MRM model for the selected input parameters is given at the end of Appendix A. These results were obtained using MRMPC.

MRTM COMPUTER PROGRAM

The computer program for the MRTM is written in Fortran; it consists of a source (or a main) program and three subroutines: SMRTM, TRIDM, and INTEG. The source program outlines the DIMENSION and COMMON statements, the READ statements for the input parameters, the WRITE statements for the output data, and carries out the overall step-by-step sequence of program calculations. In addition, it calculates the time steps and incremental distances that satisfy the stability and convergence criteria (Pinder and Gray 1977) for the numerical solution for each given problem.

Subroutine SMRTM performs all computations of the finite-difference approximations for the convection-dispersion equation and the retention equations. It also calculates the coefficients needed for the set of equations at each iteration and for each time step. Subroutine TRIDM provides a solution for a set of linear equations using the Thomas algorithm (Pinder and Gray 1977) for tridiagonal matrix-vector equations as obtained in the numerical solutions outlined above. TRIDM is called by subroutine SMRTM. INTEG is an integration subroutine for equally spaced variables; it is called by the source program to calculate the mass balance (input vs output) at specified times as desired.

The input and output variables used in the MRTM are given in Tables 3-3 and 3-4, respectively. For convenience, variables that are common to both the multireaction model (MRM) and the MRTM were given the same names in both computer codes.

Two versions of the MRTM are available: one is for use with mainframes and the other with personal computers. The input data section of the program is at the end of the code for the mainframe version, where the appropriate values for the input parameters must be provided by the user.

Table 3-3. List of input parameters required for MRTM.

Card number	Column number	Format	Variable name	Definition
I	1-80	20A4	USER	User's name or any other information (optional)
II	1-80	20A4	SOIL	Soil name or any other information (optional)
III	1-80	20A4	SOLUTE	Solute species or other information (optional)
VI	1-80	20A4	DATE	Date, experiment number, or any other information (optional)
1	51-70	E20.6	TH	Soil moisture content (Θ), $\text{cm}^3 \text{cm}^{-3}$
2	51-70	E20.6	ROU	Soil bulk density (ρ), g cm^{-3}
3	51-70	E20.6	COL	Thickness of the soil profile (L), cm
4	51-70	E20.6	WFLX	Water flux (v), cm hr^{-1}
5	51-70	E20.6	CI	Initial solute concentration in soil solution (C_i), mg L^{-1}
6	51-70	E20.6	CS	Applied solute concentration in soil solution (C_o), mg L^{-1}
7	51-70	E20.6	D	Dispersion coefficient (D), $\text{cm}^2 \text{hr}^{-1}$
8	51-70	E20.6	KD	Distribution coefficient (K_d), $\text{cm}^3 \text{g}^{-1}$
9	51-70	E20.6	NEQ	Freundlich reaction order (b), dimensionless.
10	51-70	E20.6	K1	Rate coefficient (k_1), hr^{-1}
11	51-70	E20.6	K2	Rate coefficient (k_2), hr^{-1}
12	51-70	E20.6	W	Order of reaction, (n), dimensionless
13	51-70	E20.6	K3	Rate coefficient (k_3), hr^{-1}
14	51-70	E20.6	K4	Rate coefficient (k_4), hr^{-1}
15	51-70	E20.6	U	Order of reaction (m)
16	51-70	E20.6	KS	Irreversible rate coefficient (k_s), hr^{-1}
17	51-70	E20.6	K5	Rate coefficient (k_5), hr^{-1}
18	51-70	E20.6	K6	Rate coefficient (k_6), hr^{-1}
19	51-53	I3	IT	Number of iterations (r)
20	51-70	E20.6	TPULSE	Duration of pulse (t_p), hr
21	51-70	E20.6	TTOTAL	Total simulation, hr
22	51-70	E20.6	TPRINT	Time interval for printout, hr
23	51-70	E20.6	DX	Initial guess for the depth increment (Δx), cm
24	51-70	E20.6	DT	Initial guess for the time step (Δt), hr

Table 3-4. List of output variables used in MRTM.

<i>Variable</i>	<i>Definition</i>	<i>Units</i>
TIME	Simulation time	hr
V/V0	Pore volumes of effluent (V/V_0)	dimensionless
C/C0	Relative concentration in effluent solution (C/C_0)	dimensionless
X	Soil depth (x)	cm
C	Solute concentration (c)	mg L ⁻¹
TOTAL	Total amount of solute retained per unit volume (s)	mg cm ⁻³
S1	Amount of s_1	mg kg ⁻¹
S2	Amount of s_2	mg kg ⁻¹
S3	Amount of s_3	mg kg ⁻¹
SIR	Amount of s_{irr}	mg kg ⁻¹
SEQ	Amount of s_e	mg kg ⁻¹
SINP	Total amount of applied solute (input pulse) per unit area	mg cm ⁻²
TSWATR	Total amount of solute in soil solution in soil profile	mg cm ⁻²
TSEQ	Total amount sorbed in equilibrium phase (s_e) in soil profile	mg cm ⁻²
TSKIN1	Total amount sorbed in kinetic phase (s_1) in soil profile	mg cm ⁻²
TSKIN2	Total amount sorbed in kinetic phase (s_2)	mg cm ⁻²
TSKIN3	Total amount sorbed in kinetic phase (s_3)	mg cm ⁻²
TSIR	Total amount sorbed in irreversible phase (s_{irr})	mg cm ⁻²
TEFFL	Total amount in effluent	mg cm ⁻²
BAL	Mass balance of solute	C_0

A program listing of the computer code of the PC version of MRTM is given in Appendix B. The PC version is interactive and allows the user to choose to enter the required input data in one of two ways: interactively through the keyboard, or by providing the name of an existing file that contains the input data. An example of an input data file (MRTMPC.DAT) for use with the PC version is included in the appendix. The input parameters listed in MRTMPC.DAT were used for the sensitivity analysis presented in Figure 3-5. An example of MRTM output calculations obtained using MRMPC and the input parameters in MRTMPC.DAT is included at the end of Appendix B.

To use the compiled MRTM file, the user need only to type MRTMPC to run the program. You will then be prompted for the name and destination of an output file where all model calculations will be stored. If you choose to provide the input data interactively, you will also be prompted to enter the appropriate input parameters in the order given in the data file. For convenience, ranges of values for soil parameters and reaction-rate coefficients is provided. The range of values given represents averages of soil properties and the rate coefficients; they are presented in subsequent chapters.

If you make a mistake in entering an input value, we recommend that you terminate the program and run the model again by typing MRTMPC.

Changes should not be made to the MRTM computer code unless it is absolutely necessary. The most commonly encountered modifications are to the DIMENSION statements. As written, the program code prescribes an array size of 500 for all declared variables (c , s_1 , s_2 , etc.) This represents the number of nodal points along the soil profile N where $N = \Delta x/L$. The size of incremental step Δx also depends on the value of flux v and dispersion coefficient D , which must satisfy the stability and convergence criteria (Pinder and Gray 1977) for the numerical solution of the finite-difference form of the convection-dispersion transport equation. Adjustments of the array size may be necessary for large values of v or L . Further modifications of the computer code are only necessary if additional reactions or other changes in the model configuration must be incorporated. Otherwise, the rest of the code should not be changed.

Chapter 4. Describing CR(VI) and CD Retention in Soils Using the Multireaction Model

The transport of reactive solutes through the soil profile into groundwater is a major environmental concern. Models that can predict the transport of reactive solutes through soil profiles are needed. Such models must include the reactions of the solutes in the soil, especially retention-release reactions with soil surfaces.

Over the last 30 years or so, many researchers have tried to quantify the processes governing the interactions of various solutes (e.g., pesticides, nutrients, heavy metals, other toxic substances) with soils (Dowdy et al. 1982; Nelson et al. 1983; Sposito 1981, 1984). A summary of various solute reaction and transport models was presented by van Genuchten and Cleary (1979) and Travis and Etnier (1981). However, no comprehensive analysis of the recently proposed models has been carried out, and several models have yet to be validated. A general-purpose model that could be used to describe the reactions of a wide variety of soil solutes would be a valuable predictive tool. In this chapter, we present an evaluation of the multireaction model (MRM) described in Chapter 3. Model validation was achieved by evaluating its capability to describe data from batch kinetic studies of Cr(VI) and Cd retention by several soils at several initial concentrations.

THE MODEL

A comprehensive description of the multireaction approach for heavy-metal retention in soils was given in Chapter 3. For additional details see also Amacher et al. (1988). Briefly, we assumed that the solute in the soil environment is present in the soil solution (c) and in several phases representing heavy metal retained by the soil (s_e, s_1, s_2, s_3 , and s_{irr}), where c and s are expressed in mg L^{-1} and mg kg^{-1} , respectively. The sorbed phase s_e is considered as the amount of heavy metal that is sorbed reversibly and is in local equilibrium with that in soil solution phase (c) at all times where the Freundlich equation

$$s_e = K_d c^b \quad (4-1)$$

was the governing mechanism. Here, K_d is the associated distribution coefficient and b is a Freundlich parameter. In addition, the sorbed phases s_1 and s_2 were considered in direct contact with c and reversible processes of the nonlinear kinetic type govern their reactions such that

$$\rho (\partial s_1 / \partial t) = \Theta k_1 c^n - \rho k_2 s_1 \quad (4-2)$$

$$\rho (\partial s_2 / \partial t) = \Theta k_3 c^m - \rho k_4 s_2 \quad (4-3)$$

where k_1 to k_4 are the rate coefficients (hr^{-1}), ρ is the soil bulk density (g cm^{-3}), and Θ is the water content ($\text{cm}^3 \text{cm}^{-3}$). The s_1 and s_2 phases may be regarded as the amounts adsorbed on surfaces of soil particles as well as that which is chemically bound to aluminum and iron oxide surfaces or other type surfaces. Moreover, these phases may be characterized by their kinetic sorption as well as release behavior to the soil solution and are thus susceptible to leaching in the soil. The primary difference between these two phases lies not only in the difference in their kinetic behavior but also in the degree of nonlinearity as indicated by parameters n and m . Irreversible retention was considered in the model by a sink term expressed as

$$\rho (\partial s_{irr} / \partial t) = \Theta k_5 c, \quad (4-4)$$

which is a first-order irreversible kinetic process; k_s is the associated rate coefficient (hr^{-1}). Amacher et al. (1986) showed that this sink term was necessary to describe batch results for Hg, Cd, and Cr retention vs time for five different soils.

In the MRM model, the concurrent reaction that governs the process between the s_2 and s_3 phases was considered as a kinetic reaction. In fact, the s_3 phase, which is not in direct contact with that in soil solution, is considered here as that which is nonlabile, firmly held, or fixed by the soil matrix. This phase may be characterized by its slow (retention and release) reactions. Therefore, it is considered here that the s_3 phase is a slow kinetic one and is less susceptible to transport in the soil profile. Moreover, a simple first-order reaction may be used to describe the slow kinetic retention of the consecutive-type reaction in the following form

$$\partial s_3 / \partial t = k_5 s_2 - k_6 s_3, \quad (4-5)$$

where k_5 and k_6 (hr^{-1}) are the reaction rate coefficients. If a consecutive reaction is included in the model, then eq 4-3 must be modified to incorporate the reversible reaction between s_2 and s_3 . As a result, the following equation,

$$\rho (\partial s_2 / \partial t) = \Theta k_3 c^m - \rho k_4 s_2 - \rho k_5 s_2 + \rho k_6 s_3, \quad (4-6)$$

must be used in place of eq 4-3.

Initial conditions used were that of applied (input) heavy metal concentrations at time zero, which closely resemble the conditions for kinetic batch experiments described below. In addition, the above initial value problem was solved using numerical approximations. Details of the solution are given in Chapter 3, and a listing of the computer code for the MRM is in Appendix A.

In subsequent sections we illustrate the relative significance of incorporating the various sorbed phases (s_1 , s_2 , and s_3) on the predictive capability of the MRM. Moreover, in the validation of the MRM model using Cr(VI) and Cd retention data, the equilibrium sorbed phase s_e was ignored (i.e., K_d was set to zero as an input parameter). As a result, our assumption here was that fully kinetic reactions govern all retention mechanisms in the MRM.

EXPERIMENTAL METHODS AND ANALYSIS

Soils

The soils used in this study are listed in Table 4-1 along with their taxonomic classification and selected chemical properties. All 10 soils were used in the Cr retention-release experiments, but only the first five were used in the Cd experiments. The soils were air-dried and passed through a 2-mm sieve before use. They were

Table 4-1. Taxonomic classification and selected chemical properties of the soils used in the metal retention-release study.

Soil	Taxonomic classification	pH	Organic matter (%)	CEC ($\text{cmol} + \text{kg}^{-1}$)	Fe_2O_3 (%)
Cecil	Clayey, kaolinitic, thermic. Typic Hapludults	5.1	0.24	3.72	10.20
Norwood	Fine-silty, mixed (calcareous), thermic. Typic Udifluvent	7.4	0.32	6.20	0.44
Olivier	Fine-silty, mixed, thermic. Aquic Fragiudalf	6.4	0.99	8.31	1.14
Sharkey	Very-fine, montmorillonitic, nonacid, thermic. Vertic Haplaquepts	5.4	1.96	31.3	0.94
Windsor	Mixed, mesic. Typic Udipsamments	5.4	0.94	1.20	2.20
Unnamed	Calciorthid	8.1	0.46	23.15	0.83
Kula	Medial, isothermic. Typic Euthandepts	5.4	>5.00	14.15	8.88
Lafitte	Euic, thermic. Typic Medisaprist	4.1	>5.00	25.50	2.08
Molokai	Clayey, kaolinitic, isohyperthermic. Typic Torrox	5.7	1.78	11.58	13.05
Webster	Fine-loamy, mixed, mesic. Typic Haplaquoll	7.4	4.34	23.58	0.76

analyzed for pH by the 1:1 soil-water paste method (McLean 1982), for organic matter by the acid-dichromate oxidation method (Nelson and Sommers 1982), for free iron oxides by the dithionite-citrate-bicarbonate method (Mehra and Jackson 1960), and for cation exchange capacity of the acid soils by the method of Gillman (1979) and of the alkaline soils by the sum of cations method (Thomas 1982).

Reagents

Reagent-grade potassium dichromate, cadmium nitrate tetrahydrate, and calcium nitrate tetrahydrate were used. Radionuclides obtained from New England Nuclear in the form of sodium chromate in 1 N NaCl for ^{51}Cr ($1.57 \times 10^{16} \text{ Bq kg}^{-1}$) and cadmium chloride in 0.5 M HCl for $^{115\text{m}}\text{Cd}$ ($9.25 \times 10^{12} \text{ Bq kg}^{-1}$) were used as tracers to monitor the extent of Cr and Cd reactivity with the soils.

Procedure

The retention-release of Cr(VI) and Cd were studied in separate experiments using the batch method outlined by Amacher et al. (1986). Initial concentrations of Cr(VI) in the solutions reacted with the soils were 1, 2.5, 10, 25, 50, 75, 100, 150, and 200 mg L^{-1} . Initial concentrations of Cd were 0.016, 0.026, 0.066, 0.116, 0.516, 1.02, 5.02, 10.0, 50.0, and 100.0 mg L^{-1} . The background solution composition for the Cr and Cd solutions was 0.005 M $\text{Ca}(\text{NO}_3)_2$. The radionuclides were added to the solutions to follow the extent of the retention-release reactions. The concentrations of ^{51}Cr and $^{115\text{m}}\text{Cd}$ used were $7.4 \times 10^5 \text{ Bq L}^{-1}$ and $1.5 \times 10^5 \text{ Bq L}^{-1}$, respectively.

The retention experiments were carried out as follows. Duplicate 4.0-g samples of each soil were added to preweighed 50-mL polypropylene centrifuge tubes. Forty mL of each Cr or Cd solution was added to the duplicate samples of each soil and the samples were vortex-mixed. The centrifuge tubes were placed endwise in a box on a shaker set to shake at 120 osc min^{-1} . The Cr samples were shaken 15 min every 2 hr and the Cd samples were shaken 15 min every 6 hr. After 2, 5, 8, 24, 48, 72, 96, 144, 192, 240, and 288 hr the samples were centrifuged for 5 min at 2500 rpm, aliquots of the supernatants were withdrawn for radionuclide counting, the pH of the supernatants was measured, and the samples were reweighed, vortex-mixed, and returned to the shaker. The aliquots removed for counting ^{51}Cr and $^{115\text{m}}\text{Cd}$ were 20.0 and 25.0 mL, respectively. Gamma spectrometry was used to count the 320 keV ^{51}Cr peak while $^{115\text{m}}\text{Cd}$ was determined by liquid scintillation spectrometry.

Release of retained Cr or Cd from the soil was initiated by diluting the solutions in contact with the soils. The release experiments were carried out as follows. After 336 hr of reaction between the soil samples and Cr and Cd solutions, the samples were centrifuged for 5 min at 2500 rpm, 20.0 mL of each supernatant was withdrawn of which 1.0 mL was used to count the radionuclides, the pH of the remaining supernatants was measured, and 20.0 mL of Cr- or Cd-free 0.005 M $\text{Ca}(\text{NO}_3)_2$ were added to each sample. The samples were reweighed, vortex-mixed, and returned to the shaker. The centrifuging, 20.0-mL aliquot withdrawal, pH measurements, addition of 20.0 mL of Cr- or Cd-free $\text{Ca}(\text{NO}_3)_2$ solution, reweighing, vortex-mixing, and shaking steps were repeated four times at 24-hr intervals. The samples were again centrifuged, 0.5-mL aliquots were withdrawn for radionuclide counting, the pH of the supernatants was measured, and the samples were reweighed, vortex-mixed, and returned to the shaker.

These steps were repeated four times at 48-hr intervals. Thus, both retention and release of Cr and Cd were each followed for 336 hr of reaction time. There were five dilution steps at 24-hr intervals for the release experiment and release of Cr and Cd was followed for an additional time period after the dilutions were made.

Data analysis

Details of the calculations of the amounts of Cr and Cd retained and released by the soils are outlined in Amacher et al. (1986). Concentrations of Cr and Cd in the sample solutions were calculated from the specific activities of the initial solutions and the measured activities of the sample aliquots. Correction for radionuclide decay was avoided by counting the initial solutions each time the samples were counted. The amounts of each metal retained by the soils were calculated from the difference between the initial concentrations in solution and the concentrations in solution at each sampling time with a small correction for the amounts removed for counting. The amounts of each metal released by the soils as a result of diluting the soil solutions were calculated from

the solution concentrations at each sampling time during the release experiment with a correction for the amounts remaining in the diluted solution. The amounts of each metal released by the soils after the dilution steps were calculated from the solution concentrations with a small correction for the amounts removed for counting.

The multireaction model (MRM) was used to obtain a best-fit of the retention data using a nonlinear, least-squares, curve-fitting method (van Genuchten 1981). This method is basically the maximum neighborhood method of Marquardt (1963) and is based on an optimum interpolation between the Taylor series method and the method of steepest descent (Daniel and Wood 1973). The criteria used for estimating goodness-of-fit of the model to the data were the r -square and the root mean square statistics. The root mean square is calculated by

$$rms = \{rss/(m - p)\}^{0.5} \quad (4-7)$$

where rms is the root mean square, rss is the residual sum of squares, m is the number of data points, and p is the number of parameters. The extra sum of squares principle (Kinniburgh 1986) was used to determine if there was any statistically significant improvement in the fit of the model to the data by adding more parameters (i.e., a two-reaction, three-parameter model vs a three-reaction, five-parameter model). The F -ratio needed to test the statistical significance of adding or removing parameters is calculated by

$$F(p_2 - p_1, m - p_2) = (rss_1 - rss_2)/(p_2 - p_1) / [rss_2/(m - p_2)] \quad (4-8)$$

where m , p , and rss are defined as above and the subscripts refer to the model variations. The extra sum of squares principle can only be applied if one model is a variation of another, as is the case here.

MODEL VALIDATION

Model variations

A number of variations of the multireaction model (MRM) are possible. The goodness-of-fit of six major variations of the model were tested using Cr(VI) retention data for a Windsor soil at an initial Cr(VI) concentration in solution of 1.0 mg L^{-1} ($19.2 \text{ } \mu\text{mol L}^{-1}$). The results are listed in Table 4-2. Experimental data points and model predictions for the six model variations are shown in Figure 4-1.

The five-parameter model variations (2, 4, and 5) and the seven-parameter model variation (6) provide better model predictions of these experimental data than the three-parameter model variations (1 and 3). Variation 2 (two concurrent, nonlinear reversible reactions and one concurrent, first-order irreversible reaction) provided the best overall prediction (lowest root mean square) of this data set. The standard errors of the parameter values for variation 2 are reasonable and are not inflated as a result of overfitting the model to the data.

Variations 3, 4, 5, and 6 contain a consecutive reaction (eq 4-5). In variations 3 and 5, the consecutive reaction is assumed to be irreversible, but in variations 4 and 6 a reversible consecutive reaction is assumed. The inclusion of a consecutive rather than a concurrent irreversible reaction does not improve the fit of the model to the data (variation 3 vs variation 1, variation 5 vs variation 2), nor does the inclusion of all possible reactions shown in the model (variation 6). In fact, it is not possible to determine whether the irreversible reaction is concurrent or consecutive, since both variations give the same overall fit to the data. The inclusion of an "irreversible" reaction in the model is strongly supported by the continued decrease in the solution concentration of metal during the 336 hr of reaction and the fact that not all the retained metal was released when the soil solution was diluted. These points are discussed further below. The "irreversible" reaction may have been a very slow reverse reaction, but for all practical purposes it can be considered unidirectional.

From the predictions shown in Figure 4-1, we conclude that a number of model variations can produce simulations of the data that are indistinguishable. A similar conclusion was made by Skopp (1986). It is not possible to distinguish among the possible reaction pathways by curve-fitting alone; independent experimental evidence is required. At present, we have no experimental data to indicate that the concurrent multireaction model should be used over the concurrent-consecutive version or vice versa. We chose to use the concurrent reaction version to predict the other data sets due to its simplicity, but this does not preclude the use of other versions

Table 4-2. Comparison of goodness-of-fit of several variations of the non-linear multireaction model for describing Cr(VI) retention by a Windsor soil. The initial concentration of Cr(VI) was 1.0 mg L^{-1} and the reaction order for the nonlinear reversible reactions was 0.551.

	Variation					
	1	2	3	4	5	6
Model (r^2)	0.0961	0.997	0.956	0.997	0.997	0.998
Model (rms)	0.0261	0.00791	0.0279	0.00919	0.00820	0.00865
k_1	0.256	0.331	—	—	0.331	0.330
SE	0.0289	0.0211	—	—	0.0215	0.0241
k_2	0.282	0.549	—	—	0.539	0.573
SE	0.0395	0.0635	—	—	0.0610	0.101
k_3	—	0.0221	0.253	0.362	0.0225	0.0278
SE	—	0.00682	0.0289	0.0472	0.00616	0.0149
k_4	—	0.0509	0.266	0.543	0.0428	0.0649
SE	—	0.0127	0.0378	0.140	0.0111	0.0515
k_5	—	—	0.00231	0.0336	0.00339	0.00310
SE	—	—	0.000383	0.0352	0.000423	0.00439
k_6	—	—	—	0.0664	—	0.00893
SE	—	—	—	0.0347	—	0.0537
k_7	0.00376	0.00291	—	0.00304	—	0.00235
SE	0.000448	0.000211	—	0.000205	—	0.00668

rms = root mean square.

SE = standard error of the parameter value.

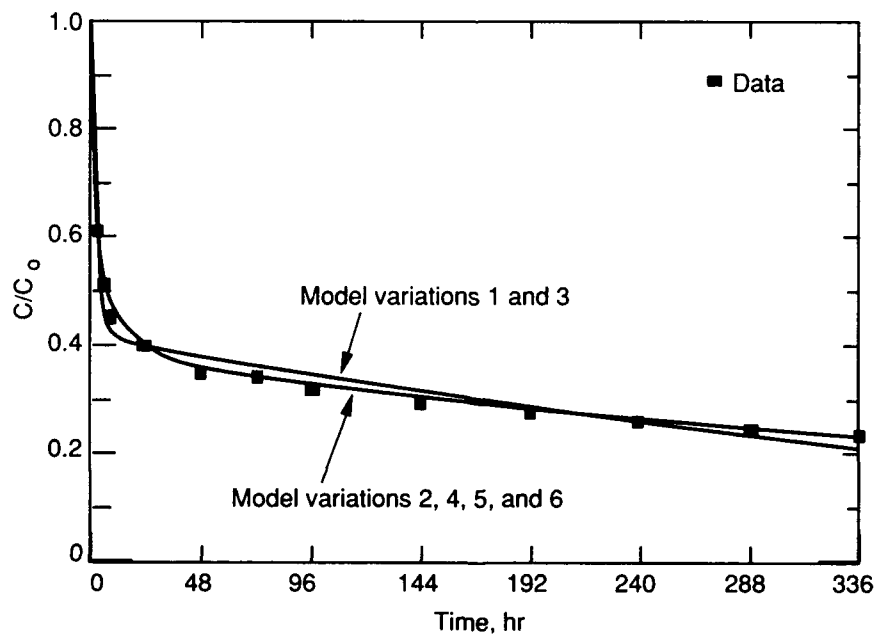


Figure 4-1. Prediction of experimental data for Cr(VI) retention by Windsor soil using six model variations. The initial concentration of Cr(VI) was 1.0 mg L^{-1} ; the reaction order of the nonlinear reversible reactions was 0.551. MRM predictions are shown as solid lines and experimental data as squares.

if independent experimental evidence warrants additional reactions. Generally, the model variation with the least number of parameters that will adequately describe the data with low parameter standard errors is the most desirable.

Cr and Cd retention kinetics

A three-parameter (one nonlinear reversible and one first-order irreversible reactions) and a five-parameter (two nonlinear reversible and one first-order irreversible reactions) version of the MRM were used to predict experimental data for the retention of Cr and Cd by several soils and at several initial solution concentrations. Selected results for several soils at one initial solution concentration and for one soil at several initial solution concentrations are listed in Tables 4-3 and 4-4 as examples for Cr and Cd, respectively. Other initial solution concentrations for the other soils gave similar results. The model was not used to fit the Cr retention data for the Norwood or Calciorthid soils because very little Cr was retained by these high-pH soils and the experimental data were too variable. Best-fit three- or five-parameter model-predicted curves are shown in Figures 4-2 to 4-5 along with the experimental data points. The five-parameter model was used in the figures only if the prediction was significantly better than the three-parameter version.

Either the three- or five-parameter model variations, depending on the initial concentration, predicted the data adequately with low standard errors for the parameters in the majority of cases (Tables 4-3 and 4-4). For

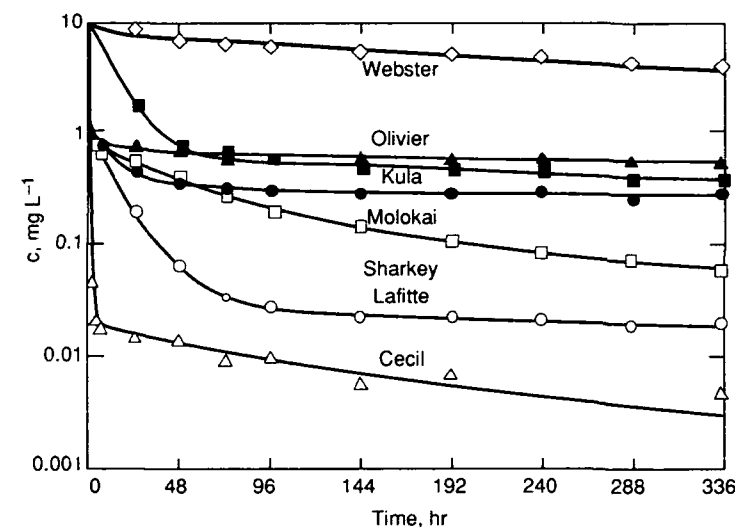


Figure 4-2. Prediction of experimental data for Cr(VI) retention by seven soils. The initial Cr(VI) concentration for the Cecil, Olivier, Sharkey, Lafitte, and Molokai soils was 1.0 mg L^{-1} ; for the Kula and Webster soils it was 10.0 mg L^{-1} . MRM predictions are shown as solid lines and experimental data as symbols.

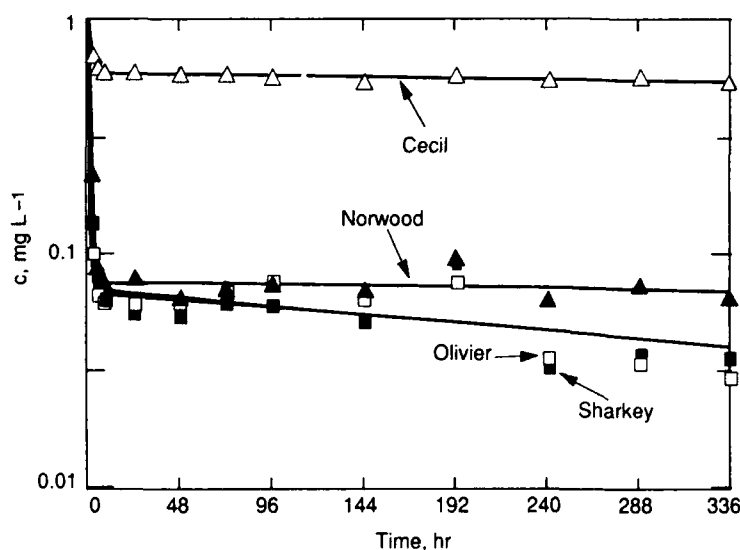


Figure 4-3. Prediction of experimental data for Cd retention by four soils. The initial Cd concentration was 1.02 mg L^{-1} .

Table 4-3. Goodness-of-fit, model parameters, parameter values, and parameter standard errors of the nonlinear multireaction model for describing Cr(VI) retention by several soils at several initial concentrations.

Soil	n	C ₀ (mg L ⁻¹)	r ²	rms	k _f	SE	k _s	SE	k _t (hr ⁻¹)	SE	k _d	SE	k _v	SE
Cecil	0.448	1.0	0.990	0.00138	0.851	0.0163	0.177	0.00693	—	—	—	—	0.211	0.0234
			0.994	0.00127	ns	0.831	0.200	0.00553	0.0655	0.0128	0.0480	0.00786	0.170	0.0339
Oliver	0.641	1.0	0.916	0.0343	0.0580	0.0128	0.151	0.0409	—	—	—	—	0.000967	0.000222
			0.985	0.0154	**	0.407	2.59	14.2	0.0104	0.00137	0.0339	0.00664	0.000605	0.000144
Sharkey	0.442	1.0	0.994	0.00884	**	0.180	0.0225	0.106	0.00722	0.000812	0.0107	0.00201	0.0102	0.00117
			0.999	0.00884	**	0.180	0.0225	0.106	0.00722	0.000812	0.0107	0.00201	0.0102	0.00117
Windsor	0.551	1.0	0.962	0.0261	0.252	0.0264	0.276	0.0360	—	—	—	—	0.00373	0.000456
			0.997	0.00791	**	0.331	0.0163	0.0300	0.0223	0.00168	0.0512	0.00528	0.00291	0.000171
	2.0	0.972	0.0459	0.264	0.264	0.0263	0.249	0.0310	—	—	—	—	0.00270	0.000301
		0.997	0.0158	**	0.432	0.0807	1.15	0.222	0.0915	0.00388	0.122	0.00660	0.00239	0.000102
	5.0	0.948	0.131	0.387	0.387	0.0517	0.326	0.0510	—	—	—	—	0.00184	0.000236
		0.992	0.0573	**	0.625	0.0737	0.784	0.0975	0.0276	0.00380	0.0515	0.00937	0.00144	0.000127
	10.0	0.973	0.155	0.352	0.352	0.0321	0.276	0.0298	—	—	—	—	0.000888	0.000106
		0.993	0.0841	**	2.19	17.8	5.50	45.1	0.151	0.00901	0.164	0.0118	0.000813	0.000054
	25.0	0.965	0.311	0.433	0.433	0.0508	0.355	0.0477	—	—	—	—	0.000573	0.000062
		0.981	0.256	ns	0.536	0.0866	0.689	0.117	0.0574	0.0108	0.118	0.0261	0.000519	0.000052
	50.0	0.806	1.12	0.477	0.477	0.145	0.402	0.138	—	—	—	—	0.000364	0.000095
		0.884	0.987	ns	5.76	773	8.23	1136	0.0516	0.0210	0.0866	0.0425	0.000277	0.000090
	75.0	0.810	1.37	0.520	0.520	0.169	0.445	0.163	—	—	—	—	0.000291	0.000071
		0.889	1.18	ns	3.11	239	4.84	378	0.0759	0.0282	0.124	0.0550	0.000235	0.000062
	100.0	0.710	1.85	0.379	0.379	0.102	0.309	0.0943	—	—	—	—	0.000131	0.000074
		0.775	1.84	ns	1.26	5.37	2.28	10.3	0.0968	0.0368	0.134	0.0602	0.000106	0.000069
Kula	0.520	10.0	0.997	0.0318	0.452	2.07	0.771	3.03	0.151	0.00309	0.0173	0.000666	0.0143	0.00141
Lafite	0.420	1.0	1.000	0.000539	2.64	42.3	5.91	94.4	0.0798	0.000441	0.0113	0.000105	0.0220	0.000762
Mohokai	0.583	1.0	0.605	0.0357	1.18	1251	1.06	1112	—	—	—	—	0.00246	0.0209
		0.997	0.002399	**	0.621	1.10	1.21	2.14	0.0207	0.000477	0.0224	0.000971	0.000467	0.000150
Webster	0.303	10.0	0.948	0.388	0.948	59889	1.03	64109	—	—	—	—	0.00258	0.00551
		0.986	0.429	ns	0.00006	2816	11.7	>10 ⁵	0.0340	0.00265	0.0219	0.00347	0.00186	0.000174

** indicates that the root mean square (rms) is significantly different at the 0.01 level of probability according to the extra sum of squares criteria.

ns = not significant

Table 4-4. Goodness-of-fit, model parameters, parameter values, and parameter standard errors of the nonlinear multireaction model for describing Cd retention by several soils at several initial concentrations.

Soil	n	C (mg L ⁻¹)	r ²	rms	k ₁	SE	k ₂	SE	k ₃	SE	k ₄	SE	k ₅	SE
Cecil	0.891	1.02	0.934	0.0118	0.292	0.0234	0.429	0.0388	—	—	—	—	0.000447	0.000094
			0.941	0.0126	ns	0.295	0.0263	0.517	0.0486	0.0172	0.00655	0.143	0.003393	0.000104
Norwood	0.812	1.02	0.961	0.00931	0.783	0.0247	0.103	0.00732	—	—	—	—	0.00307	0.00382
			0.962	0.0104	ns	0.704	0.0254	0.115	0.00695	0.0867	0.0195	0.0522	0.00179	0.00485
Olivier	0.852	1.02	0.687	0.0123	1.41	0.177	0.160	0.0283	—	—	—	—	0.0218	0.00724
			0.677	0.0161	ns	1.38	0.173	0.163	0.0262	0.0360	0.405	0.0739	0.0226	0.00671
Sharkey	0.925	1.02	0.756	0.0152	1.15	0.101	0.105	0.0177	—	—	—	—	0.0217	0.00971
			0.759	0.0172	ns	1.11	0.101	0.114	0.0168	0.0603	0.0620	0.0435	0.0209	0.0139
Windor	0.839	0.016	0.976	0.000329	0.149	0.00920	0.119	0.0121	—	—	—	—	0.00527	0.00109
			0.997	0.000130	*	0.122	0.00756	0.362	0.0281	0.0674	0.00220	0.0639	0.00395	0.000462
	0.026		0.957	0.000673	0.171	0.0135	0.137	0.0169	—	—	—	—	0.00539	0.00119
			0.981	0.000490	*	0.144	0.0265	0.488	0.105	0.0851	0.00627	0.0793	0.00932	0.000906
	0.066		0.976	0.00155	0.155	0.0109	0.113	0.0131	—	—	—	—	0.00585	0.00106
			0.992	0.000959	*	0.139	0.0139	0.328	0.0422	0.0613	0.00387	0.0555	0.00569	0.00473
	0.116		0.979	0.00218	0.194	0.0119	0.137	0.0128	—	—	—	—	0.00423	0.000694
			0.995	0.00112	**	0.172	0.0101	0.309	0.0229	0.0635	0.00319	0.0640	0.00335	0.000394
	0.516		0.965	0.0124	0.213	0.0171	0.148	0.0171	—	—	—	—	0.00320	0.000639
			0.980	0.0104	ns	0.199	0.0261	0.335	0.0528	0.0657	0.00742	0.0692	0.00265	0.000531
	1.02		0.955	0.0257	0.251	0.0232	0.184	0.0229	—	—	—	—	0.00293	0.000535
			0.991	0.0121	*	0.843	1.71	2.72	5.38	0.131	0.00674	0.113	0.00798	0.000750
	5.02		0.971	0.0947	0.230	0.0175	0.184	0.0180	—	—	—	—	0.00139	0.000251
			0.996	0.0401	**	0.268	0.0142	0.387	0.0230	0.0388	0.00270	0.0587	0.00544	0.000118
	10.0		0.948	0.240	0.376	0.0377	0.217	0.0280	—	—	—	—	0.00224	0.000405
			0.988	0.125	*	0.447	0.0628	0.669	0.101	0.118	0.00847	0.0975	0.00928	0.001221
	50.0		0.940	1.25	0.347	0.0466	0.259	0.0420	—	—	—	—	0.00155	0.000244
			0.983	0.736	*	2.23	12.2	4.54	25.3	0.117	0.0114	0.121	0.0147	0.00144
	100.0		0.944	1.94	1.02	0.334	0.929	0.319	—	—	—	—	0.00161	0.00136
			0.965	1.74	ns	3.00	46.1	3.22	50.1	0.0226	0.0120	0.0982	0.0623	0.000139

* and ** indicate that the root mean squares (rms) are significantly different at the 0.05 and 0.01 levels of probability, respectively, according to the extra sum of squares criteria.
ns = not significant

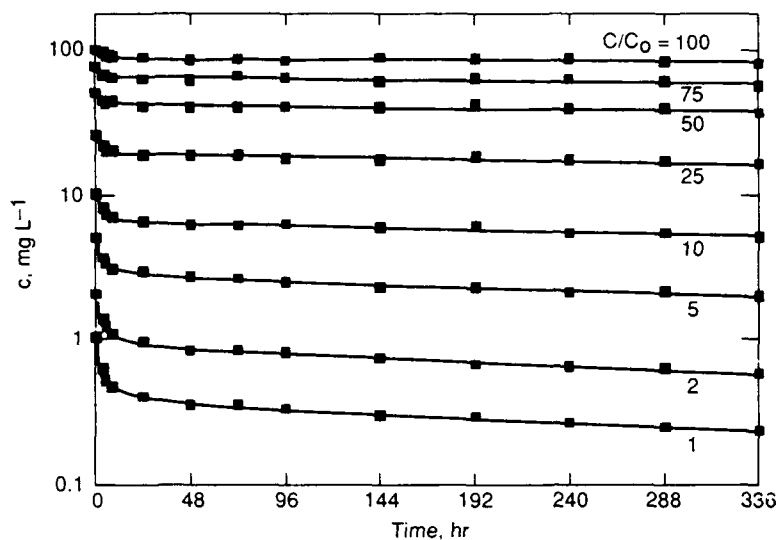


Figure 4-4. Prediction of experimental data for Cr(VI) retention by Windsor soil. The initial Cr(VI) concentrations for the top to the bottom curves were 100.0, 75.0, 50.0, 25.0, 10.0, 5.0, and 1.0 mg L^{-1} , respectively.

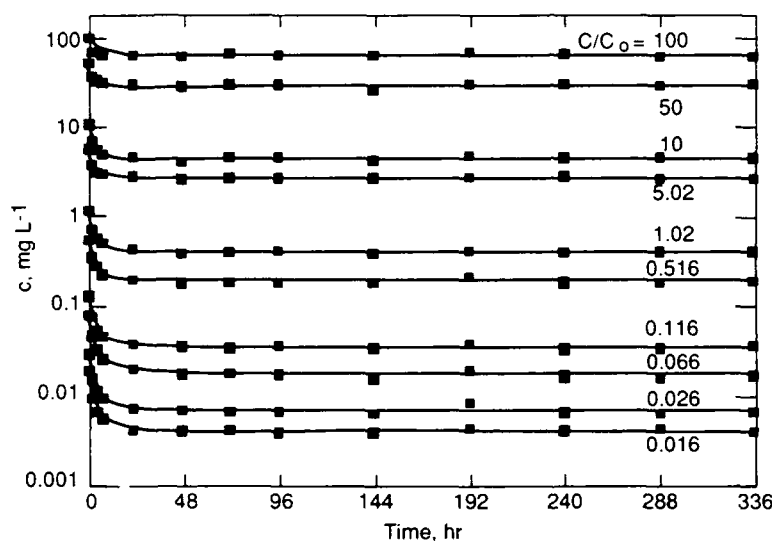


Figure 4-5. Prediction of experimental data for Cd retention by Windsor soil. The initial Cd concentrations for the top to bottom curves were 100.0, 50.0, 10.0, 5.02, 1.02, 0.516, 0.116, 0.066, 0.026, and 0.016 mg L^{-1} , respectively.

data sets where the model could not be fit to the data, a poor fit of the model to the data was obtained. Where unacceptably high parameter standard errors were obtained, a number of reasons can be cited:

- The model is an inaccurate representation of the reactions that occur.
- The model underfit the data (too few parameters).
- The model overfit the data (too many parameters).
- The experimental data was too variable, and/or
- There were too few data points.

Each of these points is discussed below with supporting examples.

The model is an inaccurate representation of the reactions that occur: it does not describe accurately Cr retention in the Kula and Webster soils at low concentrations, indicating the need for a different model for these soils. The MRM could not be fit to the data for Cr retention by the Kula and Webster soils at an initial solution concentration of 1.0 mg L^{-1} . Furthermore, the parameter standard errors for the three- and five-parameter model predictions for Cr retention by the Webster soil at an initial concentration of 10.0 mg L^{-1} are greatly inflated (Table 4-3).

The three-parameter model underfit the data. The three-parameter version of the MRM did not predict the Cr retention data for the Olivier, Sharkey, and Molokai soils ($C_0 = 1 \text{ mg L}^{-1}$) and the Windsor soil ($C_0 = 1.0, 2.0, 5.0, \text{ and } 10.0 \text{ mg L}^{-1}$) as well as the five-parameter model did, nor did it predict the Cd retention data for the Windsor soil ($C_0 = 0.016, 0.026, 0.066, 0.116, 1.02, 5.02, 10.0, \text{ and } 50.0 \text{ mg L}^{-1}$) as well.

The five-parameter model overfit the data. In most of these cases, the better fit of the five-parameter model was achieved without significantly increasing the uncertainty in the parameter estimates, but in some cases the better fit was achieved only with significant increases in the parameter standard errors. In many cases, however, where the five-parameter version could not significantly improve the fit of the model to the data, the parameter standard errors in the five-parameter version were inflated over those in the three-parameter version.

The experimental data was too variable. In the case of Cr retention by the Windsor soil, the three-parameter version worked best at higher solution concentrations and the five-parameter version worked best at the lower concentrations. At higher concentrations, only one nonlinear reversible reaction along with the first-order irreversible reaction is needed to describe the data. This does not mean that an additional nonlinear reversible reaction is not occurring at the higher concentrations. If the extent of one of the reversible reactions is minor, then it will not be observable at the higher concentrations.

Additional data points would be needed for these soils to produce reliable coefficients for the fastest reaction. The MRM could not be fit satisfactorily to the Cr retention data at initial concentrations of 150 and 200 mg L⁻¹ because of data variability. In general, the model did not predict the experimental data at higher concentrations as well as at lower concentrations because of more variability in the experimental data. In addition, at higher concentrations less time-dependent retention of Cr was observed. Moreover, the MRM did not work as well for Cr retention by the Kula, Lafitte, Molokai, and Webster soils as it did for the other soils. Aside from the need for a different model to describe Cr retention by the Kula or Webster soils, another reason for the poorer fit in these cases is that fewer data points were available for model prediction. Nine data points were taken for these soils, while 12 points were taken for the other soils. The first data point for the Kula, Lafitte, Molokai, and Webster soils was taken at 24 hr, compared to 2 hr for the other soils. Thus, the standard errors of the rate coefficients for the fastest nonlinear reversible reaction are large, since this reaction had reached equilibrium by the time the first data point was taken.

The reaction order used for the nonlinear reversible reactions was obtained from the slope of regression lines for log S vs log C after 336 hr of reaction time (Amacher et al. 1986). It was found that the slope of log S vs log C was less than 1 and did not change substantially with time after about 24 hr of reaction time. It was assumed that the faster reversible reactions attained equilibrium within 24 hr, so that the reaction order for these reactions could be calculated using the Freundlich approach (see eq 4-1). It was also assumed that all the reversible reactions had the same reaction order ($n = m$). The model allows for the possibility that they are different ($n \neq m$). At this time there does not appear to be a suitable experimental method by which the faster reversible reactions can be separated and their reaction orders determined independently, nor is it known whether they are indeed different or the same. This should be the subject of additional research.

The shapes of both the experimental data curves and the MRM predictions (Fig. 4-4 and 4-5) are influenced by the initial metal concentration in solution and clearly illustrate that nonlinear (n and $m \neq 1$) and kinetic-type retention reactions occurred. This behavior might also be attributed to possible changes in reaction mechanisms as the initial concentration changes. Furthermore, the magnitudes of the rate coefficients in Tables 4-3 and 4-4 depend on the initial concentration. This indicates that although the model is successful in describing kinetic data for a given initial concentration, the same rate coefficients cannot be used to describe data for substantially different initial concentrations. Thus, the model is an oversimplification and does not provide a complete description of the actual processes that occur during retention-release of metals by soils. It describes only the time-dependence of the concentration of metal in solution and the amounts retained by the various assumed reaction sites. In addition, only the loss of metal from solution was experimentally measured. Other components in the reactions, such as the concentrations of the reaction sites and any ionic species exchanged by the retained metal ions, were not measured. For a complete kinetic rate law, the time dependence of these components must be described successfully. Thus, the model must be considered as a representation of an apparent rather than a mechanistic rate law.

Release of Cr and Cd

The MRM indicates that a fraction of the retained metal will be released to solution because the nonlinear reactions are considered reversible. The model also indicates that another fraction of retained metal will not be

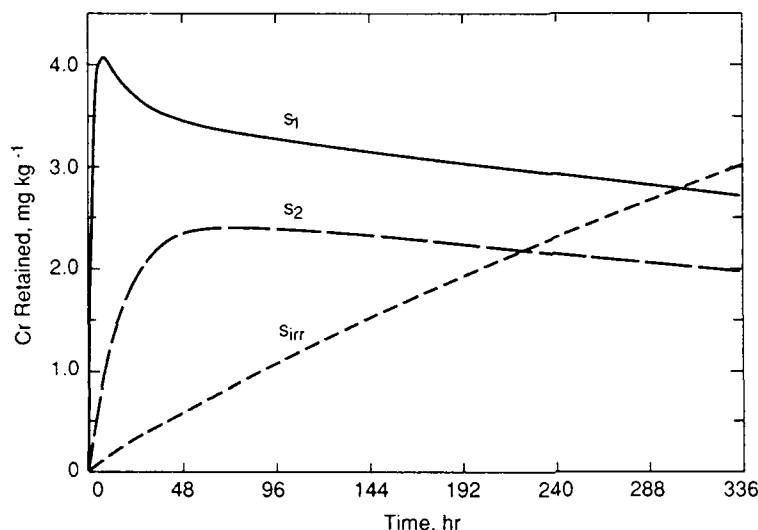


Figure 4-6. MRM predictions of the time-dependent amounts of Cr retained by three phases (s_1 , s_2 , and s_{irr}) of a Windsor soil. The initial Cr(VI) concentration was 1.0 mg L^{-1} , and the reaction order for the nonlinear reversible reactions was 0.551.

released to solution because of the irreversible retention reaction. The time-dependence of the amount of Cr ($C_0 = 1.0 \text{ mg L}^{-1}$) retained by the individual soil phases (s_1 , s_2 , and s_{irr}) for the Windsor soil is shown in Figure 4-6 as an example. According to the model, some of the Cr originally retained by s_1 and s_2 was released to solution and subsequently retained by s_{irr} . As expected, s_1 reached maximum retention prior to the highly time-dependent s_2 , while s_{irr} continued to increase with time.

Since the kinetic retention study showed that the overall retention of Cr and Cd did not reach complete equilibrium after 336 hr of reaction, we can expect that the retention of these metals will not be fully reversible. Therefore, both the model and the retention data indicate that release of metal from the soil as a result of dilution of the soil solution cannot restore equilibrium if the reversible reactions have not yet attained equilibrium (Selim et al. 1976) or if there is an irreversible reaction.

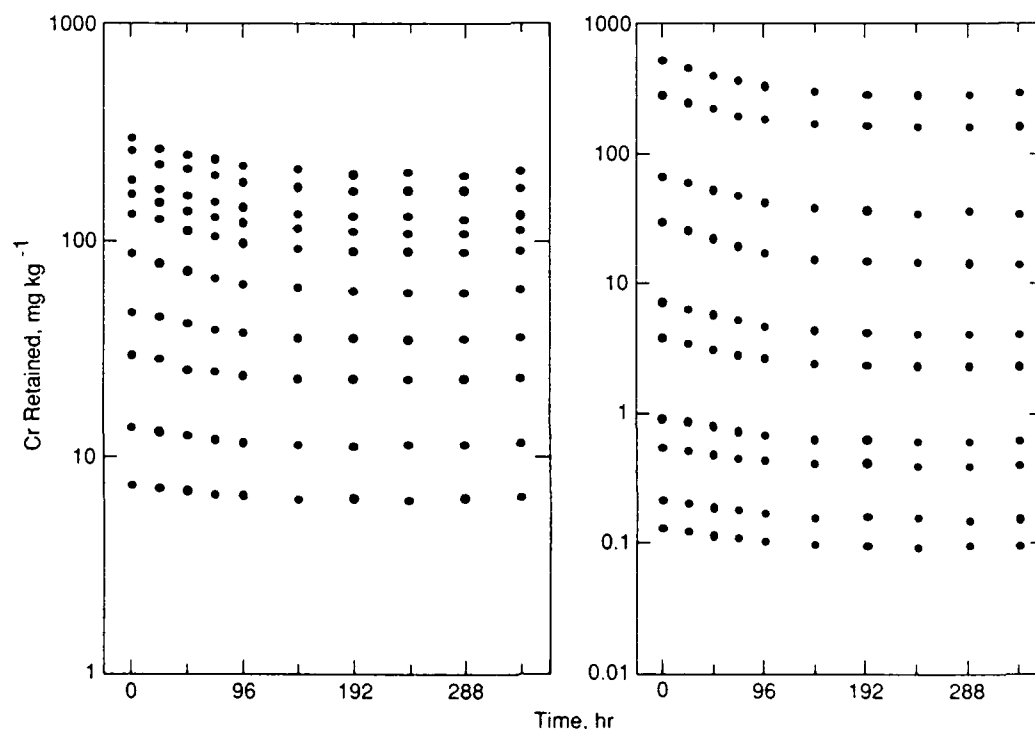


Figure 4-7. Time-dependent release of Cr and Cd from a Windsor soil at several initial concentrations of retained metal.

This finding is supported by the experimental release data. Using the Freundlich model, Amacher et al. (1986) showed that when the soil solutions were diluted, the experimental data points did not define a single retention-release isotherm, nor did they overlie the 336-hr retention data isotherm that would be required for a single reversible reaction at equilibrium. This hysteresis effect in sorption isotherms, which occurs during release and upon dilution of the soil solution, was rigorously discussed by Selim et al. (1976) and has been observed by other investigators (Elrashidi and O'Connor 1982a,b; Peek and Volk 1985). The cumulative amounts of metals released as reported by Amacher et al. (1986) indicated that substantial quantities of Cr and Cd were irreversibly retained by the soils and not released to solution even after 336 hr of release time. Furthermore, most of the retained Cr could not be extracted with 0.01 M KH_2PO_4 , which has been shown to readily replace exchangeable Cr(VI) anions (James and Bartlett 1983). Most of the retained Cd could not be extracted with 0.5 M $\text{Ca}(\text{NO}_3)_2$, which indicates that much of the Cd was not exchangeable with Ca ions.

Additional insight into the reversibility of the retention of Cr and Cd can be gained by examining Figures 4-7 and 4-8. In Figure 4-7, the amounts of Cr and Cd retained by the Windsor soil are plotted as a function of time for several initial concentrations. The amounts of retained Cr and Cd at time zero for the release experiment

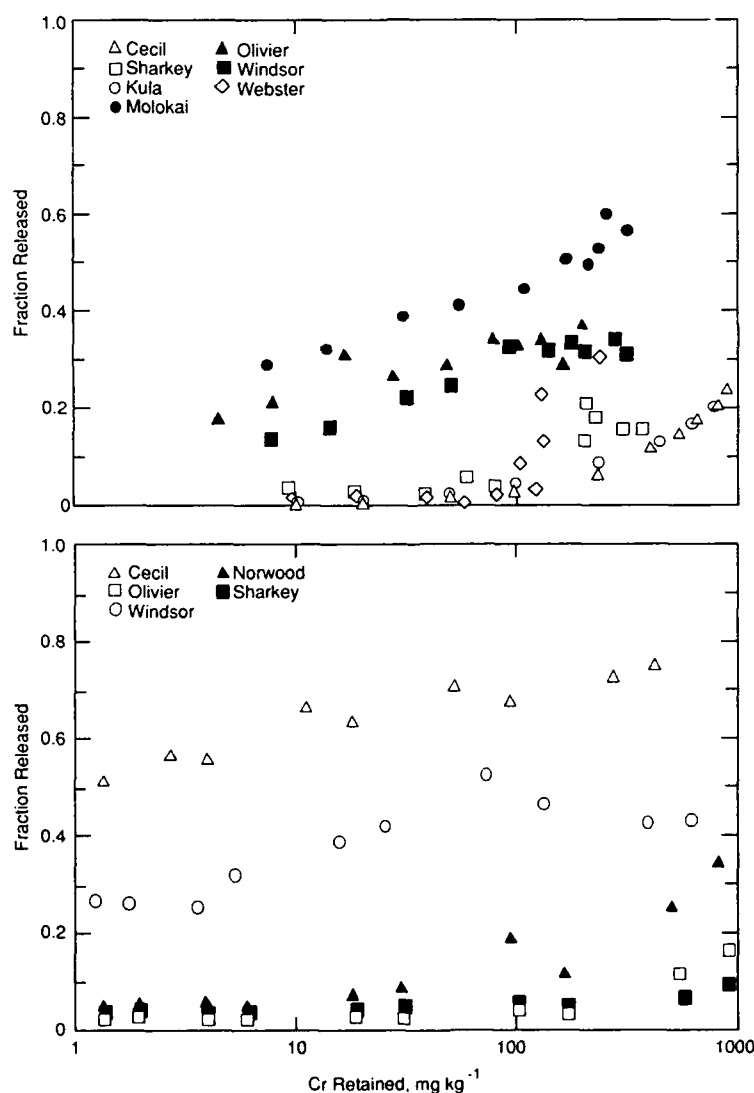


Figure 4-8. Cumulative amounts of (top) Cr and (bottom) Cd released from several soils as a function of the initial amount of metal retained by the soils at the start of metal release.

represent the amounts retained at the end (336 hr) of the retention experiment. Release of Cr and Cd occurred only during the dilution phase of the release study (24–144 hr) (Figure 4-7). After 144 hr of release no further dilutions were done and the overall retention–release of metal appeared to have reached a steady state, since little additional concentration changes were observed.

Release of metal occurred primarily when the samples with the greatest amounts of retained metal were diluted (Figure 4-7). Little release occurred at the lower concentrations. The extent of release is thus dependent upon the amount of retained metal. This can be readily seen in Figure 4-8 where the cumulative amounts of metal released over 336 hr are plotted as a function of the initial amount of metal retained by the soil at the start of the release experiment. In general, the cumulative amount of metal released increases as the amount of metal that was originally retained increases. A possible interpretation is that at lower concentrations the metal ions are retained by sites where they are more strongly held, whereas at higher concentrations they are retained by sites where they are more weakly held. There may be a range of metal-binding sites with different binding energies. This can only be verified by independent experimental evidence, not by curve-fitting of a particular model.

Sensitivity analysis

The preceding examples show how the MRM can be used to describe experimental kinetic data. At this point it is worthwhile to consider how sensitive the results of the model are to the various model parameters. Figure 4-9 shows the effect of incorporating different parameters into the model. The effect is primarily in the change of the shape of the c vs time curves. The magnitude of such a change is determined entirely by the magnitudes of the model parameters. In some cases the effect may be large, while in others it is negligible. Recall that it was possible to fit a number of model variations to the same experimental data set so that the results were virtually indistinguishable. Thus there appears to be a number of combinations of model parameters and variations that produce nearly the same results, so a unique solution of our model for its prediction of a given data set should not be expected.

The effect of changing the reaction order associated with s_1 and s_2 on model simulation curves is shown in Figure 4-10. By decreasing the reaction order, the rate of the reaction is increased. For three curves shown in Figure 4-10 the reaction orders for both nonlinear reversible reactions are the same ($n = m$), while for others the reaction orders are different. The effect of the magnitude of the rate coefficients on the simulation curves for

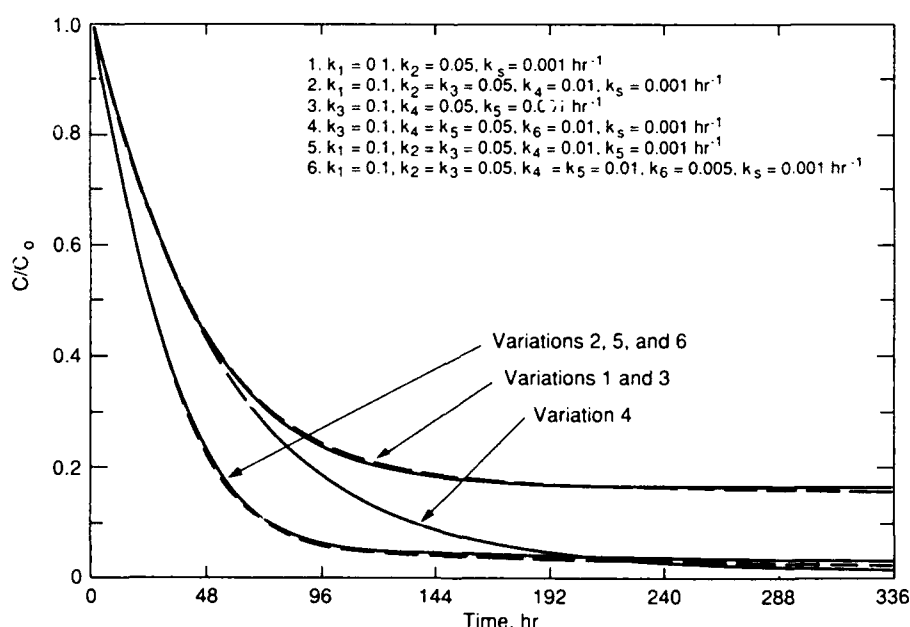


Figure 4-9. Effect of model variations on model simulations. The parameters incorporated into each model variation and their magnitudes are shown in the figure legend. The reaction order for the nonlinear reversible reactions was 0.5.

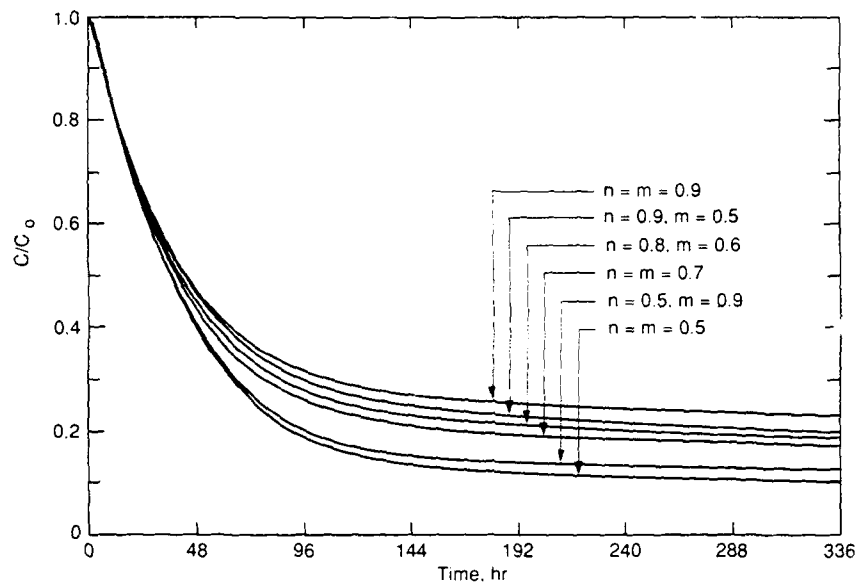


Figure 4-10. Effect of reaction order on model simulations. The reaction orders used in the model simulations are shown in the figure legend. The magnitudes of the rate coefficients were $k_1 = 0.1$, $k_2 = 0.05$, $k_3 = 0.01$, $k_4 = 0.005$, and $k_5 = 0.001 \text{ hr}^{-1}$.

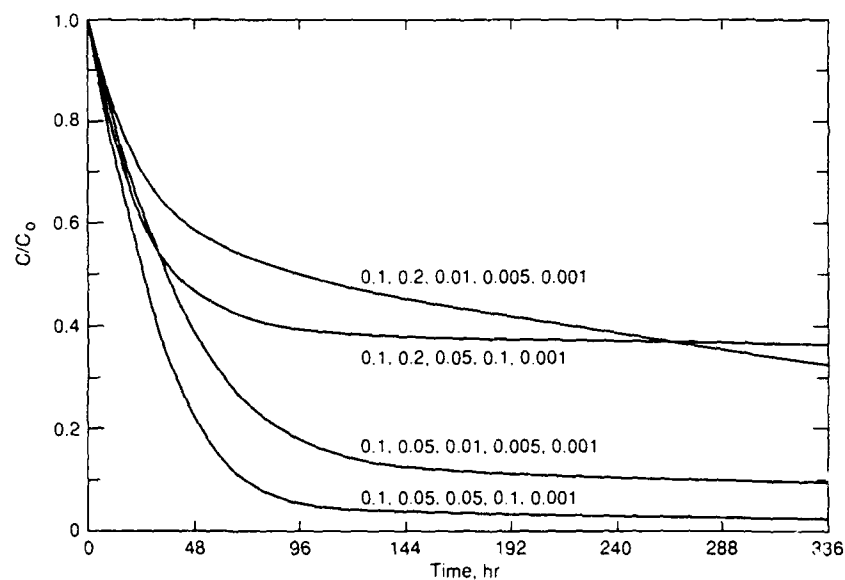


Figure 4-11. Effect of rate coefficients on model simulations. The reaction order for the nonlinear reversible reactions was 0.5.

a given model variation is shown in Figure 4-11. As the magnitudes of the rate coefficients decrease, so do the reaction rates. By adjusting the rate coefficients, an almost infinite array of curve shapes is possible. Note that in Figures 4-9, 4-10, and 4-11, the curves are not appreciably affected by the model parameters at short reaction times. Only at longer times do the curves become separated.

Mechanism consistent with model

As previously discussed, it is not possible to deduce reaction processes that occur when soils retain metal ions based solely on model predictions of the loss of metal ions from solution data. Alternative processes may

give rise to the same experimental observations. This point was discussed by Skopp (1986) in his review of time-dependent processes in soils. Sposito (1986) pointed out that the complexity of the processes that occur when ions are retained by soils defies unambiguous interpretation by simple models. The physical and chemical processes that comprise reaction mechanisms occur at the molecular level, but experimental observations on soil systems are nearly always at the macroscopic level. Furthermore, reaction mechanisms can never really be proved, only disproved if suitable experiments can be designed to rule out unambiguously a particular mechanism.

Despite these difficulties, mechanisms can be proposed that are consistent with the model and experimental observations. Harter (1984) proposed that the most rapid reversible retention reaction was nonspecific ion exchange, whereas the slower retention reaction was specific sorption of metal ions by soil surfaces. These reactions may also be interpreted in terms of formation of outer-sphere and inner-sphere complexes with soil surfaces (Sposito 1984). This interpretation is entirely compatible with the MRM model. Harter's experimental data was taken at very short time intervals using a batch reactor (Zasoski and Burau 1978). The method used in this paper is only suitable for highly time-dependent or slow reactions. However, the applicability of the model is independent of the time-scale of the experiments, since there is probably a continuum of reactions covering a wide time period. The model curve must still pass through the data points regardless of when they are taken, although the fastest reactions may be complete before the first data point is taken.

Amacher et al. (1986) proposed that the irreversible or very slowly reversible retention of Cr, Cd, and Hg may be precipitation or coprecipitation, internal diffusion, or, in the case of Cr and Hg, a change in the chemical species (oxidation or reduction). Mendoza and Barrow (1987) proposed that the continuing reaction between phosphate and soils is the penetration of adsorbed phosphate into the adsorbing surface. This would be identical to the internal diffusion process, which was also proposed by Aringhieri et al. (1985) to explain why a single second-order reversible reaction could not adequately describe Cu and Cd retention kinetics. However, actual identification of the chemical species and reaction sites is necessary to distinguish among the various possibilities, and such independent experimental evidence is for the most part lacking in the case of reactions at soil surfaces. Greater progress has been made in studying reactions at pure mineral surfaces (Davis and Hayes 1986). Nevertheless, the reaction mechanism proposed by Harter (1984) and extended to include other processes by Amacher et al. (1986) is fully consistent with a vast body of soil chemistry literature, and the MRM is compatible with this interpretation.

Chapter 5. Retention Kinetics of Mercury in Soils Using the Multireaction Model

Numerous papers have examined various aspects of the geochemistry of mercury in water, sediment, and soil (Hem 1970, Jenne 1970, Klein and Goldberg 1970, Thomas 1971, Cranston and Buckley 1972, Frost and Bisque 1972, Gavis and Ferguson 1972, Thomas 1972, Lindberg and Harriss 1974, Reimers and Krenkel 1974, Crecelius et al. 1975, Schindler and Alberts 1977, Anderson and Smith 1977, Eganhouse et al. 1978, Hogg et al. 1978, Gambrell et al. 1980, Harsh and Doner 1981). A few general conclusions can be drawn from these studies. Mercury (Hg) can be involved in a complex series of chemical and biological reactions in natural environments. Many of these reactions involve changes in the oxidation state of Hg. The chemistry of Hg in water, sediment, and soil is intimately linked to the organic matter in those phases. Organic matter appears to be the single most important component in the environment that controls the chemistry of Hg, including retention and oxidation state transformations. Retention of Hg by soil and sediment occurs by sorption onto manganese oxides (Lockwood and Chen 1973), iron oxides (Kinniburgh and Jackson 1978, Inoue and Munemori 1979), clay (Newton et al. 1976), and organic matter (Creclius et al. 1975, Eganhouse et al. 1978) and by precipitation of sulfides (Harsh and Doner 1981).

Methylation, reduction, and volatilization are the more important reactions involving changes in Hg speciation. Methylation of Hg(II) occurs in anaerobic and aerobic environments and appears to be both a biological and an abiological reaction (Langley 1973; Jacobs and Keeney 1974; Rogers 1976, 1977). Rogers (1977) showed that fulvic acid can methylate Hg(II), but humic acid cannot. Thus, abiotic methylation of Hg(II) is a potentially important reaction. Reduction and volatilization is microbially mediated and apparently does not occur abiotically (Rogers 1979, Rogers and McFarlane 1979). Avotins and Jenne (1975) also report that Hg volatilization involves microbes. However, Alberts et al. (1974) showed that humic acid could reduce and volatilize Hg(II).

It is apparent from the foregoing discussion that the reactions of Hg in the soil environment are quite complex and can involve several chemical species of Hg and retention by several solid phases in soils. Thus, multireaction models are needed to describe the chemistry of Hg in soils, especially where retention by multiple phases is occurring. Recently, Amacher et al. (1988) showed that a nonlinear multireaction model could successfully describe the time-dependent retention of chromium (VI) and cadmium by soils. The success of this model indicates that it has potential applicability in describing Hg retention reactions in soils involving a single Hg species. In a previous paper Amacher et al. (1986) showed that single-reaction models failed to describe adequately the kinetics of HgCl_2 retention by soils. In this chapter we test the ability of the multireaction model (MRM) to describe the time-dependent reactions of mercuric chloride by several soils at several initial concentrations. A complete description of the multireaction retention model (MRM) was presented in Chapter 3. In Chapter 4, the MRM was evaluated for the prediction of Cr(VI) and Cd retention in several soils. In this chapter, we discuss the major differences in model predictions for Hg and those obtained previously for Cr(VI) and Cd.

EXPERIMENTAL AND DATA ANALYSIS

Soils

Soils used in this study are listed in Table 5-1 along with their taxonomic classification and selected chemical properties. The soils were air-dried and passed through a 2-mm sieve before use. The methods used to obtain the chemical property data are given in Amacher et al. (1988).

Table 5-1. Taxonomic classification and selected chemical properties used in the Hg retention-release studies.

Soil series	Classification	pH	Organic matter (%)	CEC (cmol+ kg ⁻¹)	Fe ₂ O ₃ (%)
Cecil	Clayey, kaolinitic, thermic Typic Hapludult	5.1	0.24	3.7	10.2
Norwood	Fine-silty, mixed (calc.), thermic, Typic Udipluvent	7.4	0.32	6.2	0.44
Olivier	Fine-silty, mixed, thermic Aquic Fragiudalf	6.4	0.99	8.3	1.14
Sharkey	Very fine, montmorillonitic, nonacidic, thermic Vertic Haplaquept	5.4	1.69	31.3	0.94
Windsor	Mixed, mesic, Typic Udipsamment	5.4	0.94	1.2	2.20

Reagents

Reagent-grade mercuric chloride, calcium chloride dihydrate, and potassium dichromate were used. A radionuclide of Hg (²⁰³Hg, 3.56 × 10³ Bq kg⁻¹, HgCl₂ in 0.5 M HCl) was used as a tracer to follow the extent of the Hg retention reactions.

Procedure

Retention and release of HgCl₂ was studied using the batch method outlined by Amacher et al. (1986). Initial solution concentrations of Hg were 0.007, 0.012, 0.052, 0.102, 0.502, 1.00, 5.00, 10.0, 50.0, and 100.0 mg L⁻¹ in 0.005 M CaCl₂. The ²⁰³Hg concentration in each solution was 7.4 × 10⁵ Bq L⁻¹.

Calculations using species formation constants given by Lindsay (1979) revealed that, at the chloride and mercury concentrations used in this experiment, dissolved HgCl₂ was the predominant species. Thus, the retention of essentially a single Hg species was being studied. To help maintain oxidizing conditions and to inhibit reduction and volatilization of the Hg(II), the solutions also contained 0.005% Cr(VI). The intent was to keep Hg in a single form in solution throughout the course of the experiment.

The retention experiment was carried out as follows. Duplicate 4.0-g samples of each soil were added to pre-weighed 50-mL Teflon centrifuge tubes. Then 40 mL of each Hg solution was added to the duplicate samples of each soil, and the samples were vortex-mixed. The centrifuge tubes were placed endwise in a box on a shaker set to shake at 120 osc min⁻¹. The samples were shaken for 15 min every 6 hr. After 2, 5, 8, 24, 48, 72, 96, 144, 192, 240, and 288 hr, the samples were centrifuged for 10 min at 1300 × g. 25.0 mL of each supernatant was withdrawn for radionuclide counting, the pH of the supernatant was measured, and the samples were reweighed, vortex-mixed, and returned to the shaker.

Release of retained Hg from the soils was initiated by diluting the solutions in contact with the soils. After 336 hr of reaction between the soil samples and Hg solutions, the samples were centrifuged for 5 min at 1300 × g. 20.0 mL of each supernatant was withdrawn (of which 1.0 mL was used to count the ²⁰³Hg), the pH of the remaining supernatant was measured, and 20 mL of Hg-free 0.005 M CaCl₂ were added to each sample. The samples were reweighed, vortex-mixed, and returned to the shaker. The centrifuging, 20.0-mL aliquot withdrawal, pH measurements, addition of 20.0 mL of Hg-free CaCl₂ solution, reweighing, vortex-mixing, and shaking steps were repeated four times at 24-hr intervals. The soil samples were again centrifuged, 0.5 mL aliquots of each supernatant were withdrawn for radionuclide counting, the pH of the supernatant was measured, and the soil samples were reweighed, vortex-mixed, and returned to the shaker.

These steps were repeated four times at 48-hr intervals. Thus, both the retention and release of Hg were each followed for 336 hr of reaction time. There were a total of five dilution steps at 24-hr intervals for the release

experiment, and release of Hg was followed for an additional time period after the dilutions were made.

The activity of ^{203}Hg was counted by liquid scintillation spectrometry. Correction for radionuclide decay was avoided by counting the aliquot of the original Hg solutions each time samples were counted. To correct for losses of Hg due to sorption onto the Teflon tubes and volatilization from solution, 40 mL of each Hg solution was added to 50-mL Teflon centrifuge tubes without soil in them, and these soil-free samples were carried through the entire experimental procedure. These corrections proved to be minor.

Data analysis

Details of the calculations of the amounts of mercury retained and released by the soils are outlined in Amacher et al. (1986). Concentrations of mercury in the sample solutions were calculated from the specific activities of the initial solutions and the measured activities of the sample aliquot. The amounts of Hg retained by the soils were calculated from the differences between initial concentrations in solution and the concentrations in solution at each sampling time, with a small correction for the amounts removed for counting. The amounts of Hg released by the soils as a result of diluting the soil solutions were calculated from the solution concentrations at each sampling time during the dilution steps, with a correction for the amounts remaining in the diluted solution. The amounts of Hg released by the soils after the dilution steps were calculated from the solution concentrations at each sampling time, with a small correction for the amounts removed for counting.

The rate coefficients for the nonlinear multireaction model were obtained using a nonlinear, least-squares, parameter-optimization method (van Genuchten 1981). This method is basically the maximum neighborhood method of Marquardt (1963) and is based on an optimum interpolation between the Taylor series method and the method of steepest descent (Daniel and Wood 1973). The criteria used for estimating goodness-of-fit of the model to the data were the r-square and the root mean square statistics. The extra sum of squares principle (Kinniburgh 1986) was used to determine if there were any statistically significant improvement in the fit of the model to the data by adding more parameters to the model (e.g., one vs two nonlinear reversible reactions). Additional details have been given in Chapter 4 and are also available in Amacher et al. (1988).

MODEL EVALUATION

The reaction order for the nonlinear reversible reactions was obtained from the slope of regression lines for $\log \text{total } s (s_1 + s_2 + s_{\text{irr}})$ vs $\log c$ after 336 hr of reaction (Amacher et al. 1986). An example is shown in Figure 5-1 for the Cecil soil. Results from the other soils provided similar figures. The slope of $\log s$ vs $\log c$ at each reaction time was <1 (nonlinear) and did not change significantly with time after about 24 hr of reaction time. It was assumed that the reversible reactions attained equilibrium after 24 hr, so that an estimate of the reaction order for these reactions could be obtained using the linear form of the Freundlich equation ($\log s = \log K + n \log c$). It was also assumed that the reaction orders for all reversible reactions had the same numerical value ($n = m$), although the model allows for the possibility that they have different values. However, there does not appear to be a suitable experimental method to determine the actual number of reversible reactions and their reaction orders and rate coefficients separately and independently.

The results of the parameter optimization method for obtaining the rate coefficients are listed in Table 5-2. The fit of the model to the data is illustrated in Figures 5-2 through 5-6 for the five soils. Two variations of the model were used in describing the data: a three-parameter version (k_1, k_2, k_s) consisting of only one nonlinear reversible reaction (eq 3-2), an irreversible first-order reaction (eq 3-4), and a five-parameter version (k_1, k_2, k_3, k_4, k_s) consisting of two nonlinear reversible reactions (eq 3-2 and 3-3)

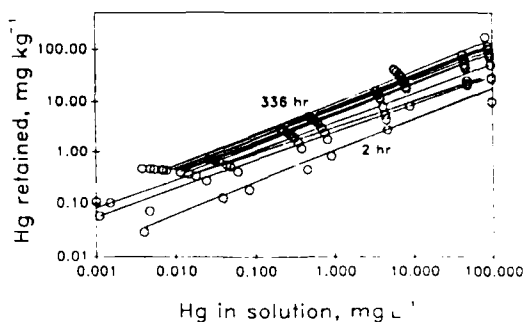


Figure 5-1. Mercuric chloride retention isotherms for Cecil soil at each sampling time from 2 to 336 hr.

Table 5-2. Nonlinear multireaction model parameters for mercury retention.

Soil	n	C_0 (mg/L)	P	r^2	r_{ms}	k_1	CI	k_2	CI	k_3 (hr ⁻¹)	CI	k_4	CI	k_5	CI
Cecil	0.515	0.052	3	0.991	0.00108	0.0383	0.0053	0.127	0.029	—	—	—	—	0.0115	0.0028
		0.10	3	0.976	0.00305	0.0392	0.0079	0.116	0.032	—	—	—	—	0.00272	0.00137
		0.50	3	0.903	0.0260	0.042	0.0218	0.104	0.067	—	—	—	—	0.00110	0.00104
		1.00	3	0.975	0.0248	0.0443	0.0136	0.100	0.038	—	—	—	—	0.00125	0.00043
		5.00	3	0.977	0.0856	0.0407	0.0160	0.0857	0.0411	—	—	—	—	0.000704	0.000207
		10.0	3	0.968	0.222	0.142	0.048	0.148	0.060	—	—	—	—	0.00102	0.00030
		50.0	3	0.942	0.589	0.173	0.215	0.458	0.635	—	—	—	—	0.000399	0.000090
		100.0	3	0.897	1.69	0.0512	0.110	0.103	0.279	—	—	—	—	0.000343	0.000141
	0.677	0.052	3	0.998	0.000259	0.162	0.010	0.120	0.015	—	—	—	—	0.129	0.022
		0.10	3	0.997	0.000509	0.219	0.011	0.0955	0.0115	—	—	—	—	0.0948	0.0189
Narwood		0.50	3	0.968	0.0133	0.258	0.042	0.0434	0.0252	—	—	—	—	0.00164	0.0512
		1.00	3	0.993	0.0187	0.136	0.028	0.0355	0.0184	—	—	—	—	0.0429	0.0291
		5.00	5	0.999	0.0473	0.153	0.030	0.198	0.063	0.0335	0.0180	0.0073	0.0048	0.0270	0.0133
		10.0	5	0.994	0.123	0.512	0.101	0.319	0.091	0.244	0.062	0.0210	0.0103	0.0332	0.0355
		50.0	5	0.998	0.555	0.246	0.062	0.280	0.087	0.0202	0.0055	0.0083	0.0065	0.00451	0.00229
		100.0	5	0.998	0.830	0.464	0.155	0.603	0.220	0.0230	0.0036	0.0150	0.0065	0.00262	0.00050
	0.786	0.052	3	0.805	0.000308	0.648	0.099	0.0710	0.0286	—	—	—	—	0.152	0.115
		0.10	3	0.988	0.000418	0.479	0.043	0.078	0.0171	—	—	—	—	0.227	0.072
		0.50	3	0.925	0.0111	0.465	0.102	0.0592	0.0400	—	—	—	—	0.0749	0.0994
		1.00	3	0.997	0.00589	0.440	0.056	0.0210	0.0063	—	—	—	—	0.00708	0.0649
Olivier		5.00	5	1.000	0.0162	0.163	0.005	0.0109	0.0019	0.186	0.016	0.146	0.023	0.0625	0.0092
		10.0	3	0.999	0.0456	0.542	0.085	0.0142	0.0037	—	—	—	—	0.00105	0.0592
		50.0	5	0.999	0.366	0.350	0.034	0.222	0.032	0.0288	0.0065	0.0106	0.0062	0.0191	0.0033
		100.0	5	0.999	0.579	0.391	0.036	0.301	0.036	0.0292	0.0027	0.0115	0.0035	0.00647	0.00111
	0.662	0.10	3	0.989	0.000271	0.378	0.034	0.201	0.032	—	—	—	—	0.358	0.071
		0.50	3	0.980	0.00577	0.308	0.090	0.142	0.054	—	—	—	—	0.259	0.129
		1.00	5	0.994	0.0121	0.705	0.584	4.05	3.41	0.189	0.105	0.0444	0.0345	0.150	0.127
		5.00	5	0.997	0.0496	0.368	0.074	0.290	0.085	0.128	0.051	0.0165	0.0093	0.0520	0.0346
		50.0	5	1.000	0.239	0.755	0.046	0.267	0.022	0.0870	0.0066	0.0131	0.0025	0.00802	0.00191
		100.0	5	0.999	0.541	0.815	0.066	0.308	0.031	0.0633	0.0048	0.0135	0.0031	0.00422	0.00091
Windbor		0.10	3	0.988	0.00254	0.0559	0.0176	0.155	0.099	—	—	—	—	0.0712	0.0258
		0.50	3	0.975	0.0205	0.0830	0.0282	0.113	0.067	—	—	—	—	0.0137	0.0050
		1.00	3	0.977	0.0370	0.113	0.032	0.119	0.052	—	—	—	—	0.00974	0.00304
		5.00	3	0.986	0.137	0.116	0.029	0.0841	0.0279	—	—	—	—	0.00370	0.00090
		10.0	3	0.984	0.304	0.268	0.070	0.128	0.046	—	—	—	—	0.00636	0.00141
		50.0	3	0.985	0.868	0.166	0.062	0.124	0.056	—	—	—	—	0.00133	0.00022
	0.546	0.10	3	0.952	2.28	0.174	0.109	0.127	0.095	—	—	—	—	0.000793	0.000245
		0.50	3	0.952	2.28	0.174	0.109	0.127	0.095	—	—	—	—	0.000793	0.000245
		1.00	3	0.952	2.28	0.174	0.109	0.127	0.095	—	—	—	—	0.000793	0.000245
		5.00	3	0.952	2.28	0.174	0.109	0.127	0.095	—	—	—	—	0.000793	0.000245

n = reaction order, C_0 = initial concentration, P = number of model parameters, r_{ms} = root mean square, CI = 95% confidence interval

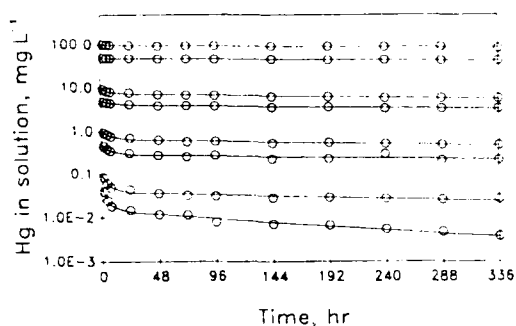


Figure 5-2. Time-dependent HgCl_2 retention by Cecil soil. The data points are shown as circles and the model as a solid line.

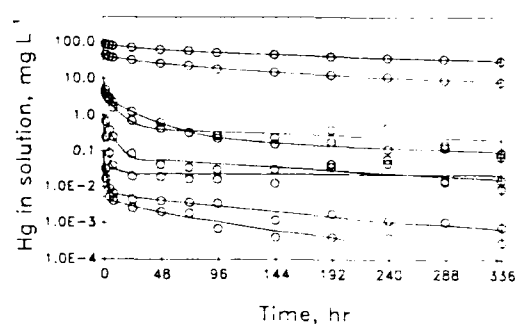


Figure 5-3. Time-dependent HgCl_2 retention by Norwood soil.

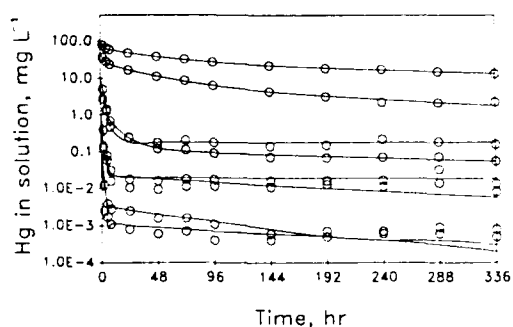


Figure 5-4. Time-dependent HgCl_2 retention by Olivier soil.

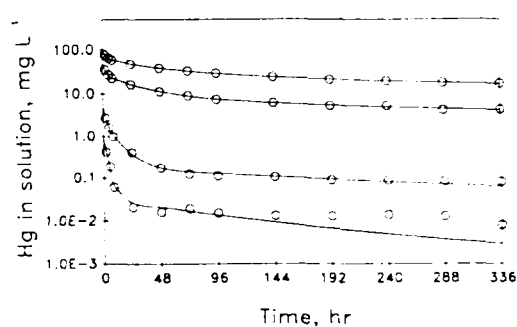


Figure 5-5. Time-dependent HgCl_2 retention by Sharkey soil.

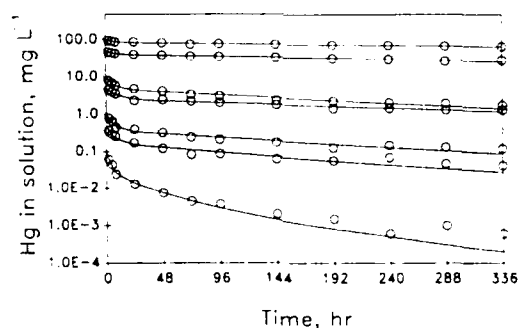


Figure 5-6. Time-dependent HgCl_2 retention by Windsor soil.

and the irreversible first-order reaction (eq 3-4). The five-parameter version is reported in Table 5-2 only if it was found to give a statistically better fit to the data than the three-parameter version according to the extra sum of squares principle. Otherwise the three-parameter version is shown.

It is apparent from the r -square and root mean square statistics in Table 5-2 and from the figures that the model describes the data quite well for the initial concentrations shown. The 95% confidence intervals for the individual rate coefficients were for the most part reasonable, except in those cases where the experimental data did not fit a smooth curve, so considerable uncertainty in the values of the rate coefficients was observed.

Some dependence of the rate coefficients on the initial Hg concentration was observed, especially when comparing values at the highest and lowest initial concentrations. The shapes of the experimental data and model curves were also dependent on the initial Hg concentration. This indicates possible changes in the number and type of retention reactions as the initial concentration changes. Since Hg is retained by a number of solid phases

in soils, it is likely that a range of other types of reaction sites is encountered. At low Hg concentrations, not all the sites will be filled, but at higher concentrations, some types of sites may be completely filled while others are only partially filled, depending on the affinity of the sites for Hg. This can account for the varying shapes of the time-dependent retention curves as the initial concentration increases. Because the model is probably a simplified representation of a complex series of reactions, the rate coefficients obtained by fitting the model to the data should not be considered those for elementary reactions that comprise the reaction mechanism. They are probably apparent rate coefficients for a number of reactions of similar type.

For the Cecil and Windsor soils, which showed the least retention of Hg, the three-parameter model was adequate for all the initial concentrations listed. The five-parameter model provided improved description of the data at the higher Hg concentrations for the Norwood, Olivier, and Sharkey soils. This behavior is quite the opposite of that observed for Cr(VI) and Cd retention by these same soils (Amacher et al. 1988), where the five-parameter version was found to work best at lower concentrations. The additional reaction needed at higher Hg concentrations may be due to the presence of other types of sorption sites not encountered (or inaccessible) at lower Hg concentrations or to the formation of an insoluble Hg phase. However, the fit of the model to the data cannot be used as proof of this since a number of retention reactions may account for the continuing loss of Hg from solution, including precipitation, internal diffusion, or some species transformation reactions. It is not necessary to postulate a specific reaction in order to use the model to describe the data, however, since it is a general-purpose model that does not rely on a specific reaction mechanism. These points were discussed in detail by Amacher et al. (1988) and Selim and Amacher (1988).

The model did not fit the data at the lowest initial Hg concentrations ($<0.052 \text{ mg L}^{-1}$ for the Cecil, Norwood, and Olivier soils and $<0.10 \text{ mg L}^{-1}$ for the Sharkey and Windsor soils; data not shown). There was some evidence of the formation of a labile Hg species at the lowest concentrations of Hg, since after an initial decrease in Hg concentration upon reaction with the soils in the retention experiment, a slow increase in Hg concentration in solution was observed over time as Hg was released from the soils back into solution. The Hg release was greatest for the Cecil soil and was much less for the other soils. The identity of this labile Hg species is unknown, but in view of the known biological and abiological methylation of Hg in soils, this is a likely possibility. Experimental methods for determining different Hg species would need to be used to determine the identity of the labile Hg observed at trace concentrations. The formation of labile Hg occurred despite the presence of 0.005% potassium dichromate, which was added to the solutions to inhibit reduction and volatilization of Hg. The concentration of this labile form of Hg was minor relative to the total Hg concentration in the solution, and its presence did not interfere with the application of the model to the data at greater than trace concentrations of Hg. Inclusion of species transformation reactions in the model would increase its usefulness at trace Hg concentrations, but rate coefficients for such reactions are lacking and need to be determined.

Incorporation of an irreversible reaction in the model (eq 4-4) is supported by the continuing loss of Hg from solution. Complete equilibrium was not attained in 336 hr of reaction. The retention of Hg was not fully reversible, as illustrated by Figure 5-7, which shows the time-dependent release of Hg from the Cecil soil. The other soils showed similar results. It is apparent that there was little

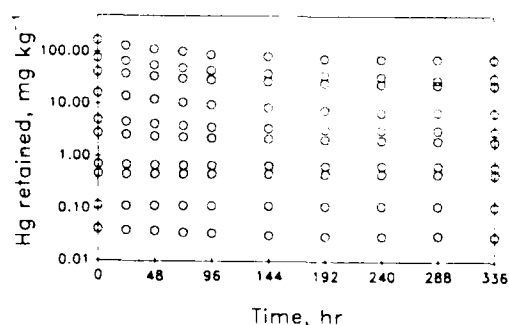


Figure 5-7. Time-dependent mercury release from Cecil soil.

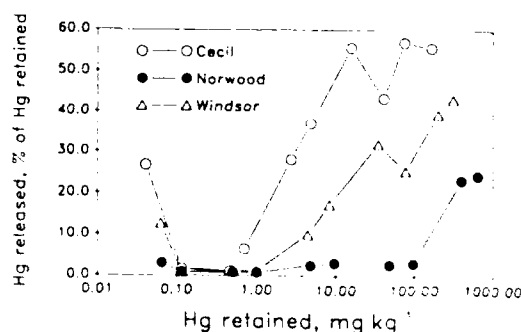


Figure 5-8. Cumulative mercury release as a function of retained mercury.

if any Hg release at the lower concentrations and that where release occurred, it was found primarily during the dilution steps, since little release of Hg was observed after they were discontinued. Apparently, Hg release is extremely slow or does not occur at lower concentrations.

The cumulative amounts of Hg released expressed as a percentage of the amounts retained by the soils prior to the start of the release experiment were plotted as a function of the amounts retained. Figure 5-8 clearly shows that Hg release is a function of the amount of Hg retained by the soil. Very little cumulative release of Hg occurred at the lower retained Hg levels. This supports the existence of a range of different types of retention sites with different affinities for Hg. At low amounts of retained Hg, virtually all the Hg is retained by high-affinity sites that will not readily release Hg when the soil solution is diluted. At higher levels of retained Hg, the high-affinity sites become filled and Hg is bound by lower-affinity sites that will release it when the soil solution is diluted. The various soils also show different levels of affinity for Hg. The Cecil and Windsor soils, which retained less Hg than the other soils, more readily released it to solution. The Norwood, Olivier, and Sharkey soils showed about the same affinity for Hg. Only the cumulative release of Hg from the Norwood soil is shown in Figure 5-8, since the Olivier and Sharkey soils showed nearly equivalent results and overlapped the Norwood results almost exactly.

The results of this investigation show that a nonlinear multireaction model is capable of describing the retention of a single species of Hg by multiple soil phases. The model does not depend on any particular mechanism of solute retention, because the reactions in the model are distinguished solely on the basis of reaction rate; it is not necessary to have any prior knowledge of the retention processes to describe the data successfully. However, the fit of the model to the data does not prove any particular mechanism, since multiple processes can produce the same experimental results. Independent experimental evidence is needed to identify the processes responsible for element retention in soils. The model would have to be modified to include Hg species transformation reactions, including methylation and reduction-volatilization, to describe accurately Hg retention at trace concentrations. Independently measured rate coefficients for the Hg species transformation reactions would greatly aid the use of the model, because attempting to fit too many rate coefficients at once results in a poor description of the data and yields poorly defined model parameters with excessively large standard errors.

Chapter 6. Predicting Cr(VI) Transport Based on the Multireaction and Transport Model

For several heavy metals (e.g., Cu, Hg, Cr, Cd, and Zn), retention–release reactions in the soil solution have been observed to be strongly time-dependent. Recent studies on the kinetic behavior of several heavy metals include Harter (1984), Aringhieri et al. (1985), and Amacher et al. (1986) among others. A number of empirical models have been proposed to describe kinetic retention–release reactions of solutes in the solution phase.

The earliest model is the first-order kinetic equation, which was first incorporated into the convection–dispersion transport equation by Lapidus and Amundson (1952). First-order kinetic reactions have been extended to include the nonlinear kinetic type (van Genuchten et al. 1974, Mansell et al. 1977, Fiskell et al. 1979). A variety of other kinetic reactions are given by Murali and Aylmore (1983).

Amacher et al. (1986) found that the use of single-reaction kinetic models did not adequately describe the time-dependent retention of Cr, Hg, and Cd for several initial concentrations and several soils. As a result, Amacher et al. (1988) developed a multireaction model that includes concurrent and concurrent–consecutive processes of the nonlinear kinetic type. The model was capable of describing the retention behavior of Cd and Cr(VI) over time for several soils. In addition, it predicted that a fraction of these heavy metals was irreversibly retained by the soil.

The literature search revealed that no studies were carried out on the description of heavy metals transport in soils where the retention–release reactions are based on kinetic mechanisms. Amoozegar-Fard et al. (1984) may have been the first to investigate the mobility of Cd, Ni, and Zn using a fully reversible first-order kinetic reaction. In this study, we modified the multireaction model of Amacher et al. (1988) and incorporated it into the convection–dispersion transport equation. The model's ability to predict Cr(VI) mobility in several soils was examined.

This chapter describes the transport behavior of Cr(VI) in six soils that have varying properties. We also test the ability of the multireaction and transport model (MRTM) for its ability to predict the retention characteristics of Cr(VI) during transport. In addition, we investigate the use of kinetic retention parameters obtained from batch experiments to predict Cr(VI) mobility in soils.

THE MODEL

A complete description of the multireaction approach for heavy metal transport and retention in soils (MRTM), including the appropriate initial and boundary conditions for the model and details of the numerical solution used, is given in Chapter 3. A listing of the computer code for the model is given in Appendix B.

EXPERIMENTAL METHODS

Six soils were used to investigate the interactions and mobility of Cr(VI) in soil columns. The taxonomic classification, mechanical size distribution, and selected properties of the soils are given in Table 6-1. The B horizon for the Cecil soil and the Ap horizon of all other soils were used. The kinetic retention of Cr(VI) by these soils was investigated by Amacher et al. (1988) using the batch technique for a wide range of applied Cr(VI) concentrations. Selected results from this work are given in Chapter 4.

Miscible displacement experiments were used to study the mobility of Cr(VI) in the six soils. Each soil was air-dried and passed through a 2-mm sieve before use. We followed the miscible displacement procedure described by Selim et al. (1987), where Plexiglas columns (4.4 cm in diameter \times 6.35 cm long) were uniformly packed with each soil to a given bulk density (Table 6-2). More than 20 pore volumes of 0.005 M $\text{Ca}(\text{NO}_3)_2$ were introduced into each column at a constant flux (Table 6-2) to equilibrate the soils with the background solution. A pulse of 100 mg L^{-1} Cr(VI) in 0.005 M $\text{Ca}(\text{NO}_3)_2$ solution was introduced into each column using

Table 6-1. Taxonomic classification and selected physical and chemical properties used in the miscible displacement studies.

Soil series	Classification	Sand (%)	Silt (%)	Clay (%)	pH	Organic matter (%)	CEC (cmol+ kg ⁻¹)	Fe ₂ O ₃ (%)
Cecil	Clayey, kaolinitic, thermic Typic Hapludult	30	19	51	5.1	0.24	3.7	10.2
Norwood	Fine-silty, mixed (calc.), thermic Typic Udifluvent	79	18	3	7.4	0.32	6.2	0.44
Olivier	Fine-silty, mixed, thermic Aguie Fragiudalf	5	89	6	6.4	0.99	8.3	1.14
Unnamed	Calciorthid	70	19	11	8.1	0.46	14.7	0.83
Webster	Fine-loamy, mixed, mesic Typic Haplaquoll	27	49	24	7.4	4.34	48.1	0.76
Windsor	Mixed, mesic Typic Udipsamment	77	20	3	5.4	0.94	1.2	2.20

Table 6-2. Soil parameters for the various soil columns of the miscible displacement experiments.

Soil	Column number	Water content, Θ (cm ³ cm ⁻³)	Bulk density, ρ (g cm ⁻³)	Flux, v (cm hr ⁻¹)	Cr(VI) pulse (pore volumes)
Calciorthid	101	0.47	1.41	0.14	2.6
	110	0.48	1.37	1.08	2.3
Cecil	201	0.59	1.08	0.13	15.9
	210	0.48	1.39	1.04	16.3
Norwood	301	0.42	1.72	0.14	2.5
	310	0.47	1.40	1.04	4.3
Olivier	401	0.52	1.27	0.14	2.6
	410	0.53	1.25	1.00	3.9
Webster	510	0.62	0.96	0.96	1.5
Windsor	601	0.38	1.65	0.17	4.9
	610	0.42	1.53	1.13	3.7

a peristaltic tubing pump at a constant flux. A radionuclide tracer (3.7×10^9 Bq L⁻¹ ⁵¹Cr) was added to the Cr solutions to follow the extent of the mobility and retention reactions. The radio-labeled Cr(VI) pulse was followed by several pore volumes of Cr-free background solution of 0.005 M Ca(NO₃)₂ to elute the columns and obtain a complete Cr(VI) breakthrough curve for each soil. A fraction collector was used to collect column effluent. The 320 keV ⁵¹Cr peak was counted using gamma spectrometry. In addition, for each soil at least two Cr(VI) miscible displacement experiments or replications were conducted. Soil parameters associated with each column experiment, such as v , ρ , Θ , and volume of solute pulse (input), are given in Table 6-2. The difference among replications for each soil is that significantly different fluxes (v) were used, as is commonly carried out in miscible displacement studies.

To determine the hydrodynamic dispersion coefficient (D) for each soil, a pulse of tritium (³H₂O) and chloride-36 (³⁶Cl) was applied to each column prior to the Cr(VI) pulse. The volume of each pulse was equivalent to one pore volume. For both tracers, the background solution of 0.005 M Ca(NO₃)₂ was maintained at

all times. Liquid scintillation spectrometry was used to count the chloride-36 and tritium radio-tracers.

EVALUATION OF THE MRTM

A prerequisite for the validation of a model is that the necessary model parameters be estimated independently. In this study, we attempted to utilize, whenever possible, parameters that were either independently measured or estimated by indirect means. Parameter estimates were utilized for the kinetic rate coefficients from the batch studies of Amacher et al. (1988). Selected rate coefficients are also given (see Chapter 4). Other model parameters such as v , ρ , and Θ were experimentally measured for individual soil columns.

Values for the hydrodynamic dispersion coefficient (D) of eq 3-7 were obtained independently from the tracer data for $^3\text{H}_2\text{O}$ and ^{36}Cl for each soil. Selected results of $^3\text{H}_2\text{O}$ and ^{36}Cl breakthrough curves (BTCs) are shown in Figure 6-1. These BTCs were interpreted using the classical convection-dispersion equation (Selim and Mansell 1976):

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - (v/\Theta) \frac{\partial c}{\partial x}, \quad (6-1)$$

where c = solute concentration (mg L^{-1})
 Θ = soil water content ($\text{cm}^3 \text{cm}^{-3}$)
 v = Darcy's flux (cm hr^{-1})
 D = hydrodynamic dispersion coefficient ($\text{cm}^2 \text{hr}^{-1}$)
 x = soil depth (cm)
 t = time (day^{-1})
 R = retardation factor,

$$R = 1 + \rho K_d / \Theta, \quad (6-2)$$

and K_d is the distribution coefficient ($\text{cm}^3 \text{kg}^{-1}$). Best-fit model parameters (Table 6-3) for D (and R) were obtained by use of the nonlinear least-squares optimization method of van Genuchten (1981). Estimates for R values for the tracers were close to unity for all soils. R greater than unity indicates sorption or simply retardation, whereas $R < 1$ may indicate ion exclusion or negative sorption. Similar values for R for tritium and chloride-36 were reported by Nkedi-Kizza et al. (1983), van Genuchten and Wierenga (1986), and Selim et al. (1987). Estimates for D were similar for the two tracers; therefore, a simple average value for D was used in the transport model. Tracer results of Figure 6-1 also show little tailing of the BTCs, suggesting that the local equilibrium assumption for these soils, tracers, and water fluxes is valid (Rubin 1983).

Breakthrough curves for Cr(VI) transport from the miscible displacement experiments are shown in Figures 6-2 to 6-9 for all soils. Results from Calciorthid, Norwood, and Webster soils show high peak concentrations close to unity ($C/C_0 = 1$), with a sharp rise of the influent (or left) side of the BTCs. This was accompanied by little tailing of the desorption (or right) side of the BTCs. The times of arrival (or location) of the BTCs also suggest that little retention of Cr(VI) occurred in these soils. Moreover, the overall shape of these BTCs are similar

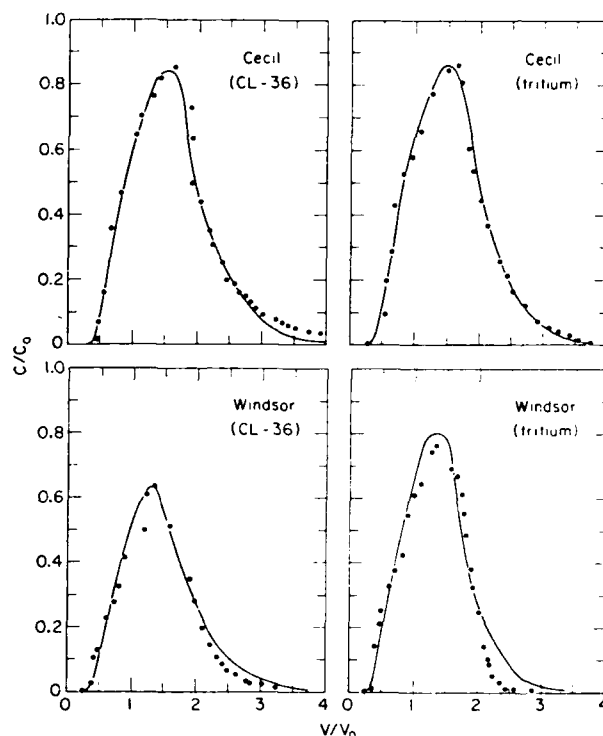


Figure 6-1. Chloride-36 and tritium breakthrough curves (BTCs) for Cecil and Windsor soils. Solid curves are model-fitted BTCs.

Table 6-3. Estimated dispersion coefficients (D) and retardation factors (R) obtained from chloride-36 and tritium breakthrough curves.

Soil series	Chloride-36 ($\times 10^{-4}$)		Tritium ($\times 10^{-4}$)	
	Dispersion coefficient ($\text{cm}^2 \text{hr}^{-1}$)	Retardation factor	Dispersion coefficient ($\text{cm}^2 \text{hr}^{-1}$)	Retardation factor
Cecil	0.172 ± 0.0474	0.991 ± 0.0496	0.173 ± 0.0429	0.934 ± 0.0409
Norwood	0.074 ± 0.0334	0.955 ± 0.0066	0.085 ± 0.0384	0.997 ± 0.0714
Olivier	0.054 ± 0.0123	0.996 ± 0.0326	0.077 ± 0.0074	1.021 ± 0.0296
Windsor	0.297 ± 0.0474	1.082 ± 0.0496	0.186 ± 0.0474	0.905 ± 0.0496
Unnamed	0.054 ± 0.0095	0.942 ± 0.0169	0.066 ± 0.0161	1.034 ± 0.0312

to those for the nonreactive chloride-36 and tritium BTCs of Figure 6-1. For Olivier soil (Fig. 6-6), the BTC has a similar overall shape to the above three soils with a high peak concentration and a moderate tailing of the desorption side. However, there is a shift to the right of the entire BTC, suggesting the occurrence of retardation (sorption-desorption) during transport in Olivier soil. Such a retardation in the arrival of Cr(VI) in the effluent was not observed for the previous three soils.

The BTC results of Figure 6-2 through 6-6 show that for Calciorthid, Norwood, Webster, and Olivier soils approximately 100% of the applied Cr(VI) pulse was recovered in the effluent solutions. In contrast, for Cecil and Windsor soils (Fig. 6-7 through 6-9), the area under the BTCs indicate that only about 30 and 60% of the applied pulse was recovered, respectively. In addition, Cecil and Windsor BTCs show extensive tailing and a retardation of Cr(VI) in the effluent as well as a lowering of concentration maxima. These features strongly suggest kinetic (reversible and irreversible) solute retention (Selim et al. 1976, Rao et al. 1979, Nielsen et al. 1986).

Reversible and irreversible reactions of Cr(VI) in these soils may be the result of several retention mechanisms, including physical adsorption, ion exchange, formation of surface complexes, precipitation, and coprecipitation (Bartlett and James 1979, Amacher and Baker 1982, James and Bartlett 1983a,b,c). Irreversible retention, which is incorporated in our model, is strongly supported by the continuing reaction between Cr(VI) and the soils even after 336 hr in the batch studies, the fact that overall retention was only partly reversible, and the fact that little retained Cr(VI) could be replaced by phosphate ions (Amacher et al. 1986). We postulate that the irreversible reaction is caused by a reduction of Cr(VI) to Cr(III), with possible precipi-

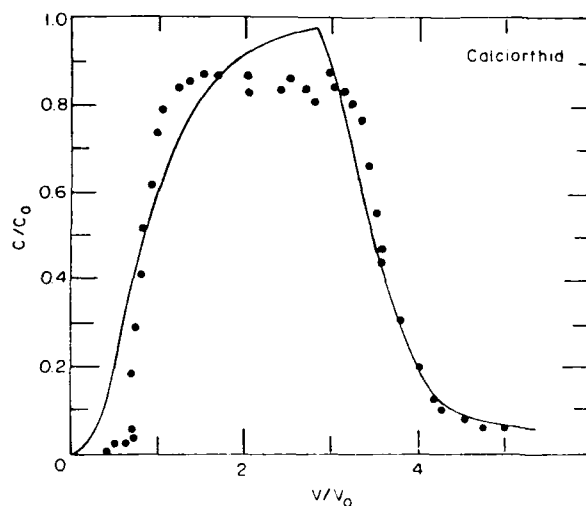


Figure 6-2. Measured (dots) and predicted BTCs for Cr(VI) in Calciorthid soil (column no. 101).

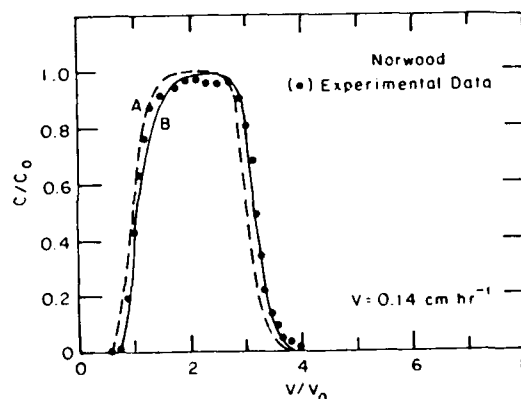


Figure 6-3. Measured (dots) and predicted BTCs for Cr(VI) in Norwood soil at $v = 0.14 \text{ cm hr}^{-1}$ (column no. 301). Curve A is the model prediction for a nonreactive solute and curve B is a fitted BTC using equilibrium (Freundlich) sorption ($K_d = 0.0475 \text{ cm}^3 \text{g}^{-1}$ and $b = 0.952$).

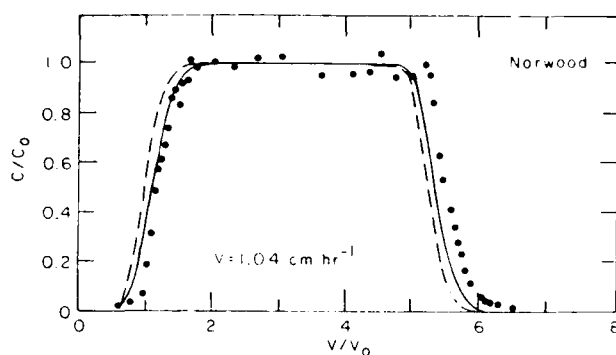


Figure 6-4. Measured (dots) and predicted BTCs for Cr(VI) in Norwood soil at $v = 1.04 \text{ cm hr}^{-1}$ (column no. 310). Dashed curve is model prediction for a nonreactive solute and solid curve is a fitted BTC using equilibrium (Freundlich) sorption ($K_d = 0.0475 \text{ cm}^3 \text{ g}^{-1}$ and $b = 0.952$).

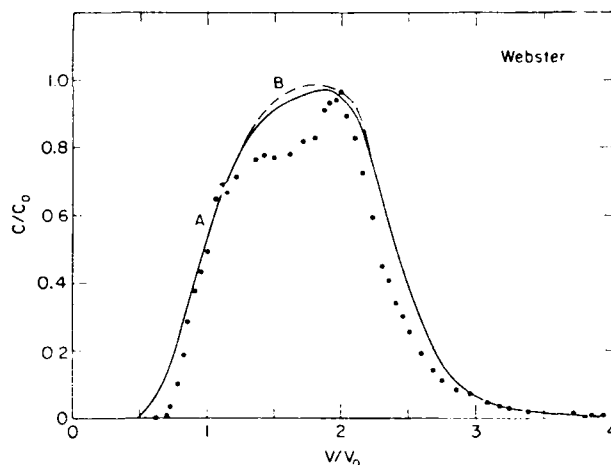


Figure 6-5. Measured (dots) and predicted BTCs for Cr(VI) in Webster soil (column no. 510). Curve A is model prediction using batch rate coefficients for $C_0 = 10 \text{ mg L}^{-1}$ and curve B (dashed) is model results for a nonreactive solute.

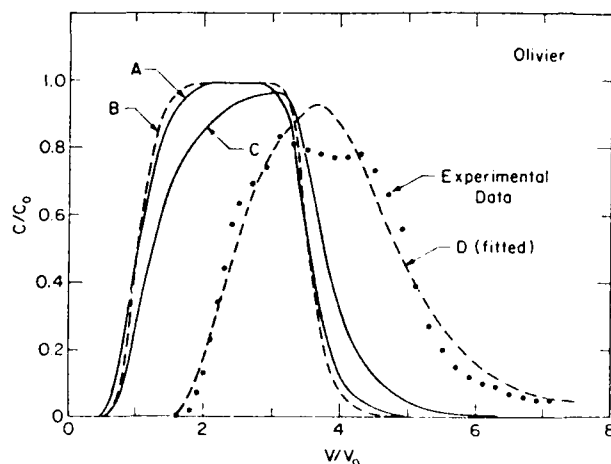


Figure 6-6. Measured (dots) and predicted BTCs for Cr(VI) in Olivier soil (column no. 401). Curves A, B, and C are model predictions using batch rate coefficients for $C_0 = 100, 10,$ and 1 mg L^{-1} , respectively. Curve D is a fitted BTC using parameters obtained from least-squares optimization.

tation of Cr(III) on mineral surfaces or as discrete particles of hydrous Cr(III) oxides. Organic matter, Fe(II) minerals, and other possible reducing agents are known to irreversibly reduce Cr(VI) to Cr(III). Reduction of Cr(VI) to Cr(III) by organic matter is a slow process at normal environmental pH and temperature levels as used in this study. Moreover, the overall reaction rate is pH-dependent (Amacher and Baker 1982), and the proposed irreversible term in the model (eq 3-13) is consistent with these observations.

The solid and dashed curves shown in Figures 6-2 to 6-9 are model calculations of Cr(VI) BTCs for the miscible displacement experiments. In the following discussion, *predicted* BTCs imply the use of independently measured model parameters derived from the batch reaction studies ($k_1, k_2, k_3, k_4,$ and k_1) of Amacher et al. (1988) that are given in Chapter 4. The predicted BTC shown in Figure 6-2 for Calciorthid was obtained with all rate coefficients set to zero. These values were selected since little or no sorption of Cr(VI) was previously measured for all applied initial concentrations in the batch experiments. Therefore, the miscible displacement

data are consistent with the data obtained earlier from the batch studies. Moreover, model predictions agreed well with the experimental BTC; consequently, Cr(VI) transport may be considered similar to that of a non-reactive solute. In fact, the sorption side of the experimental BTC indicates early arrival, which suggests a degree of negative retardation (or ion exclusion) in the Calciorthid soil. Other possible reasons for early arrival of BTCs may be the presence of preferential (micro- vs macropore) flow and/or mobile-immobile regions (van Genuchten and Wierenga 1976).

The use of a nonreactive transport model also provided good predictions of the experimental BTC for Norwood soil (Fig. 6-3). According to Amacher et al. (1988), Cr(VI) retention in Norwood was similar to Calciorthid where little sorption was detected for these high pH soils. Improved BTC prediction was obtained when the nonlinear least-squares (best-fit) optimization scheme (van Genuchten 1981) was used in conjunction with our model. As a result, the *fitted* BTC (solid curve in Fig. 6-3) was obtained, which suggests small Cr(VI) retention in this soil. Actual best-fit parameter estimates were for K_d was $0.0475 \pm 0.0236 \text{ cm}^3 \text{ g}^{-1}$ and for b 0.952 ± 0.092 . The use of linear retention (i.e., $b = 1$) provided similar BTC predictions.

To illustrate the reliability of our experimental results as well as the versatility of our model, Cr(VI) results for Norwood soil obtained under high flux ($v = 1.04 \text{ cm hr}^{-1}$, column no. 310, Table 6-2) were also examined. This is shown in Figure 6-4, where the use of a nonreactive transport model provided good agreement with the experimental results. This finding is consistent with that obtained previously for BTC results from low flux ($v = 0.14 \text{ cm hr}^{-1}$) for the same soil shown in Figure 6-3. Moreover, the use of fitted model parameters (K_d and b) from the low-flux BTC provided equally good prediction for the high-flux BTC, as indicated by the solid curve of Figure 6-4. We should also point out that analyses of BTC results for other soil columns at high fluxes (not shown) were consistent with those for Norwood soil; refer to other studies on the influence of flux on solute retention during transport in soils (e.g., Selim et al. 1976, van Genuchten and Wierenga 1986). Therefore, we limit the following discussion to Cr(VI) transport in columns under low fluxes (see Table 6-2).

The description of Cr transport for Webster soil (Fig. 6-5) was attempted in two different ways. Because of the overall shape and location of the BTC, we utilized a nonreactive model to describe the experimental data

Figure 6-7. Measured (dots) and predicted BTCs for Cr(VI) in Cecil soil (column no. 201) using the three-parameter model (i.e., $k_3 = k_4 = 0$). Curves A, B, C, D, and E are model predictions using batch rate coefficients for $C_0 = 100, 25, 5, 2$, and 1 mg L^{-1} , respectively.

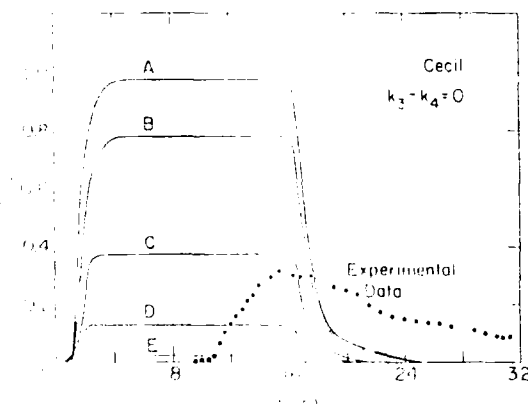
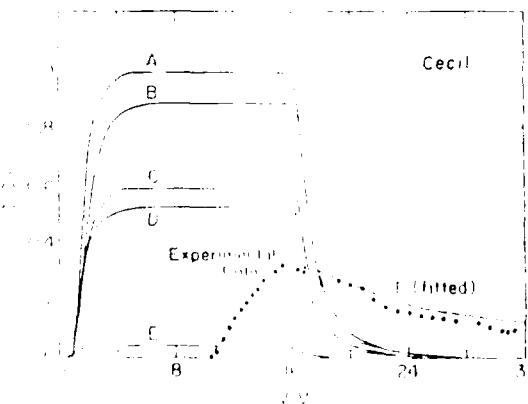


Figure 6-8. Measured (dots) and predicted BTCs for Cr(VI) in Cecil soil (column no. 201) using the five-parameter model. Curves A, B, C, D, and E are model predictions using batch rate coefficients for $C_0 = 100, 25, 5, 2$ and 1 mg L^{-1} , respectively. Curve F is a fitted BTC using parameters obtained from least-squares optimization (see Table 6-4).



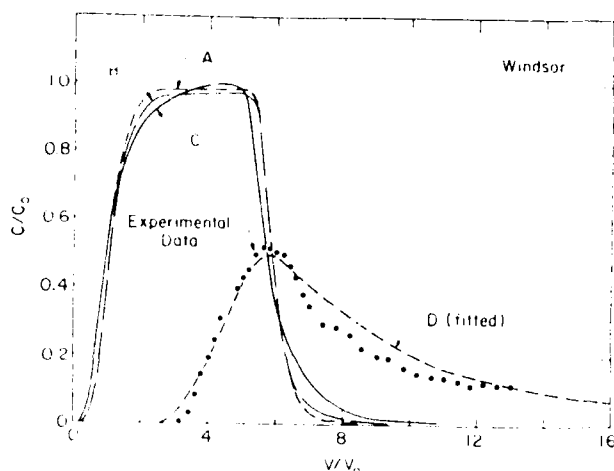


Figure 6-9. Measured (dots) and predicted BTCs for Cr(VI) in Windsor soil (column 601). Curves A, B, and C are model predictions using batch rate coefficients for $C_0 = 2, 5,$ and 100 mg L^{-1} , respectively. Curve D is a fitted BTC using parameters obtained from least-squares optimization (see Table 6-3).

applied pulse to the miscible displacement columns. Model calculations using other coefficients for different C_0 were not performed because poor parameter estimates (highly inflated standard errors) were obtained using parameter optimization. The use of the multireaction model to describe Cr retention in batch experiments was, therefore, not recommended for this soil. It is conceivable that poor parameter estimates are the result of the extremely low Cr retention or lack of kinetic reactions as indicated by the shape of the BTC in Figure 6-5.

The predicted BTCs shown in Figures 6-6 to 6-9 for Olivier, Cecil, and Windsor soils were obtained using different sets of parameter values for the rate coefficients ($k_1, k_2, k_3, k_4,$ and k_5) in the transport model. This is because a unique set of values for the rate coefficients was not obtained from the batch data; rather, a strong dependence of rate coefficients on input concentration (C_0) was observed (Amacher et al. 1988). For these soils, several features of the predicted BTCs are in common and suggest strong dependence on the set of rate coefficients used in model predictions. Increased sorption and decreased peak concentrations were predicted when batch rate coefficients from low initial concentrations (C_0) were used. The dependence of predicted BTCs on rate coefficients from different C_0 s is manifested for Cecil soil, whereas minimum influence was obtained for Windsor soil.

From Figures 6-6 through 6-9, the use of batch rate coefficients at $C_0 = 100 \text{ mg L}^{-1}$, which is the concentration of Cr(VI) in the input pulse, grossly underestimated Cr(VI) retention by the predicted BTCs for these soils. In fact, for Olivier and Windsor soils, underestimation of Cr retention and thus overestimation of potential mobility of Cr in these soils was consistently observed for all sets of rate coefficients used. However, for Cecil soil, the use of sets of rate coefficients from low C_0 s resulted in lower overall concentration in the effluent and predicted an increased retention in the soil column. This is a direct result of higher irreversible rate coefficients for Cecil in comparison with Olivier or Windsor soils. In addition, as C_0 decreased from 100 to 1 mg L^{-1} , k_5 values increased by more than two orders of magnitude (from 0.00093 to 0.211 hr^{-1}), which resulted in higher amounts of Cr irreversibly retained by the Cecil soil as predicted with our transport model.

The model predictions shown in Figures 6-6 through 6-9 clearly illustrate the failure of the proposed model to describe the transport data when independently measured model parameters were used. The reasons for this failure, which has been observed by other scientists, are not fully understood. A likely explanation is that the proposed model does not completely account for all reaction mechanisms or the reaction components present in the soil system. Specifically, the model may be an apparent rather than a complete mechanistic rate law. It is conceivable that the strong dependence of rate coefficients on C_0 , as obtained from batch experiments, may

(dashed curve). We also obtained model predictions using estimated parameters from the batch results and the three-parameter version of the multireaction model (MRM). Specifically, parameters $k_1, k_2, n,$ and k_5 given in Table 4-3 (Table 5 of Amacher et al. 1988) were used in the MRTM. Similarities of model predictions (solid curve) to the nonreactive BTC (curve A) were not surprising. This is primarily due to the large k_1 and k_2 values (0.948 and 1.08 hr^{-1}), which suggest rapid retention-release reactions and thus closely resemble conditions for local equilibrium. In addition, the extent of Cr retention was small due to the small values for the order of reaction b ($= 0.303$) and k_5 ($= 0.00258 \text{ hr}^{-1}$). The model estimated that only 0.1% of applied Cr was irreversibly retained by the soil column after 4 pore volumes. The parameters used for model calculations were the batch results for an initial concentration (C_0) of 10 mg L^{-1} , whereas a C_0 of 100 mg L^{-1} was used in the

Table 6-4. Best-fit model parameters for miscible displacement experiments for Olivier, Cecil, and Windsor soils.

Parameter	Olivier	Cecil	Windsor
K_d ($\text{cm}^3 \text{g}^{-1}$)	1.616 ± 0.1439	2.614 ± 0.1747	15.292 ± 1.1123
b	0.799 ± 0.0224	0.513 ± 0.0197	0.418 ± 0.0187
k_1 (hr^{-1})	—	74.061 ± 1.3769	2.313 ± 1.1109
k_2 (hr^{-1})	—	0.498 ± 0.0421	0.388 ± 0.2182
n	—	0.436 ± 0.2729	0.486 ± 0.1495
k_3 (hr^{-1})	—	1.334 ± 0.1162	—
k_4 (hr^{-1})	—	0.016 ± 0.0019	—
m	—	0.455 ± 0.0172	—
k_5 (hr^{-1})	—	0.0156 ± 0.00551	0.0145 ± 0.00979
r^2	0.973	0.931	0.955

also be due to additional mechanisms still ignored in the model. Invariant rate coefficients with solution concentrations are expected if a complete mechanistic rate law is postulated. Amacher et al. (1988) considered the rate coefficients to be pseudo rate coefficients.

The dependence of BTC predictions on the version of the model used to obtain the necessary rate coefficients was also examined, as depicted by the predictions shown in Figures 6-7 and 6-8 for Cecil soil. In Figure 6-7, the predictions were obtained using the three-parameter model version (i.e., $k_3 = k_4 = 0$), whereas the BTCs in

Figure 6-8 were obtained using the five-parameter version (see Amacher et al. 1988). It is evident that the use of these two different model versions resulted in different model predictions, as clearly illustrated by BTCs C and D in Figures 6-7 and 6-8. This is not always the case, however, based on predictions of retention data from the batch experiments as illustrated by Amacher et al. (1988). In fact, it was concluded that a number of model variations can produce similar model predictions of the kinetic batch results. In addition, Skopp (1986), Nielsen et al. (1986), and Selim and Amacher (1988) stated that use of alternative models to describe time-dependent reactions may give similar predictions.

An excellent fit of a data set does not in itself constitute a proof of any specific retention–release reaction. Therefore, no efforts were made in this study to examine the capabilities of different model variations based on curve-fitting alone. Instead, we utilized our transport model along with the optimization (curve-fitting) scheme to test its ability to describe the BTC from these soils without relying on parameter estimates from the batch experiments. Our hypothesis here was that a model gives an inaccurate representation of the reaction mechanism and should thus be discarded if it is completely incapable of describing experimental BTCs such as those in Figures 6-6 through 6-9. The estimated parameter values that provided best fit of these BTCs are given in Table 6-4. For all three soils, the goodness of fit as measured by r^2 exceeded 0.90 (see Table 6-4).

Despite the fact that the model was incapable of predicting the BTCs shown in Figures 6-6 through 6-9 except by the use of curve-fitting procedures, some limited interpretations of the model description of the data and associated parameters should be given. For Olivier soil the use of a nonlinear (Freundlich) equilibrium rather than kinetic retention reactions provided excellent BTC prediction with no apparent need for irreversible (sink-term) sorption from the soil solution. Less than 0.1% of applied Cr was irreversibly sorbed when batch k_{irr} values were used in BTC predictions (e.g., curves A, B, and C of Figure 6-6) and thus is in agreement with model calculations based on curve-fitting only. For Cecil and Olivier soils, it was necessary to incorporate the Freundlich equilibrium sorption in addition to kinetic-type reactions to obtain the best-fit BTCs shown. This is manifested by the large K_d estimates obtained for these two soils. Equilibrium-type sorption–desorption reactions were not incorporated in the multireaction model of Amacher et al. (1988). Most striking, based on parameter estimates given in Table 6-4, is that the order of reactions (b , n , and m) obtained based on best-fit predictions were essentially similar for each soil. Moreover, these estimated values were somewhat similar to the order of reactions obtained from batch experiments. This is particularly true for Cecil soil and to a lesser extent for Windsor and Olivier. This finding implies that one order of reaction may be capable of describing all reversible retention–release reactions and that it may be determined from data analysis of batch experiments. In addition, mechanistic models, which require fewer parameters, are extremely desirable since fewer measurements need to be performed to determine such parameters independently.

Chapter 7. A Second-Order Two-Site Retention and Transport Model

In this chapter we present an analysis of a kinetic second-order approach for the description of heavy metals retention mechanisms in the soil environment. This second-order approach will be incorporated into the non-equilibrium two-site model to simulate the potential retention during transport of heavy metals in soils. In Chapter 8 this approach will be extended to the diffusion-controlled mobile-immobile (or two-region) transport model.

A main feature of the second-order two-site (SOTS) model proposed here is the assumption that there are two types of retention sites on soil matrix surfaces and that the primary difference between them is based on the rate of the proposed kinetic retention reactions. We also assume that the retention mechanisms are site-specific, e.g., the sorbed phase on type 1 sites may be characteristically different (in energy of reaction or the identity of the solute-site complex) from that on type 2 sites. An additional assumption is that the rate of solute retention reaction is a function not only of the solute concentration present in the solution phase but of the amount of available retention sites on matrix surfaces as well.

MODEL FORMULATION

Second-order kinetics

For simplicity, we denote s_T to represent the total retention capacity or the total amount of sites on matrix surfaces. It is assumed that s_T is invariant with time. Therefore, based on the two-site approach, the total sites consist of two types such that

$$s_T = s_{T1} + s_{T2} \quad (7-1)$$

where s_{T1} and s_{T2} are the total amount of type 1 sites and type 2 sites, respectively. If F represents the fraction of type 1 sites to the total amount of sites, we thus have

$$s_{T1} = F s_T \quad \text{and} \quad s_{T2} = (1 - F) s_T \quad (7-2)$$

We now denote ϕ as the amount of unfilled or vacant sites in the soil such that

$$\phi_1 = s_{T1} - s_1 = F s_T - s_1 \quad (7-3)$$

$$\phi_2 = s_{T2} - s_2 = (1 - F) s_T - s_2 \quad (7-4)$$

where ϕ_1 and ϕ_2 are amounts of vacant sites and s_1 and s_2 are the amounts of solute retained (or the filled sites) on type 1 and type 2 sites, respectively. As the sites become filled or occupied by the retained solute, the number of vacant sites approaches zero, i.e. $(\phi_1 + \phi_2) \rightarrow 0$. In the meantime, the amount of solute retained by the soil matrix approaches that of the total capacity (or maximum amount) of sites, $(s_1 + s_2) \rightarrow s_T$.

We commonly express the amount of solute retained, such as s_1 and s_2 of eq 7-3 and 7-4, as the mass of solute per unit mass of soil (M/M soil). Therefore, based on the above formulations, the amount of total sites s_T , s_{T1} , and s_{T2} and vacant or unfilled sites ϕ_1 and ϕ_2 must also have similar dimensions. Here the units used for s and ϕ will be in terms of milligrams of solute per kilogram soil mass (mg kg^{-1}).

We propose that the retention mechanisms follow a second-order kinetic-type reaction where the forward process is controlled by the product of the solution concentration c (mg L^{-1}) and the amount

of unoccupied or unfilled sites (ϕ) (Selim and Amacher 1988). Specifically, the reactions for type 1 and type 2 sites may be expressed by the reversible processes:



and



Therefore, the differential form of the kinetic equations of the rate of solute retention may be expressed as

$$\rho \partial s_1 / t = \Theta k_1 \phi_1 c - \rho k_2 s_1 \quad \text{for type 1 sites} \quad (7-7)$$

and

$$\rho \partial s_2 / t = \Theta k_3 \phi_2 c - \rho k_4 s_2 \quad \text{for type 2 sites} \quad (7-8)$$

where k_1 and k_2 (hr^{-1}) are the forward and backward rates of reaction for type 1 sites, and k_3 and k_4 are the coefficients for type 2 reaction sites, respectively. In addition, Θ is the soil water content ($\text{cm}^3 \text{cm}^{-3}$) and ρ is the soil bulk density (g cm^{-3}). If ϕ_1 and ϕ_2 are omitted from eq 7-8 and 7-9, the above equations yield two first-order kinetic retention reactions (Lapidus and Amundson 1952). However, a major disadvantage of first-order kinetic reactions is that, as the concentration in solution increases, a maximum solute sorption is not attained, which implies that the soil has an infinite solute-retention capacity or that there is an infinite number of exchange sites on matrix surfaces. In contrast, the approach proposed here achieves maximum sorption when all unfilled sites become occupied (i.e., ϕ_1 and $\phi_2 \rightarrow 0$).

In a fashion similar to the nonequilibrium two-site concept proposed by Selim et al. (1976), type 1 sites may be regarded as those where equilibrium is rapidly reached (i.e., in a few minutes or hours). In contrast, type 2 sites are highly kinetic and may require several days or months for apparent local equilibrium to be achieved. For type 1 sites, therefore, rate coefficients k_1 and k_2 are expected to be several orders of magnitude larger than k_3 and k_4 of the type 2 sites. As $t \rightarrow \infty$, i.e., when both sites achieve local equilibrium, eq 7-7 and 7-8 yield the following expressions. For type 1 sites,

$$\Theta k_1 \phi_1 c - \rho k_2 s_1 = 0 \quad \text{as} \quad t \rightarrow \infty \quad (7-9a)$$

or

$$s_1 / (\phi_1 c) = (\Theta k_1 / \rho k_2) = \omega_1 \quad \text{as} \quad t \rightarrow \infty \quad (7-9b)$$

and for type 2 sites

$$\Theta k_3 \phi_2 c - \rho k_4 s_2 = 0 \quad \text{as} \quad t \rightarrow \infty \quad (7-10a)$$

or

$$s_2 / (\phi_2 c) = (\Theta k_3 / \rho k_4) = \omega_2 \quad \text{as} \quad t \rightarrow \infty \quad (7-10b)$$

Here ω_1 and ω_2 represent equilibrium constants for the retention reactions associated with type 1 and type 2

sites, respectively. The formulations of eq 7-9 and 7-10 are analogous to expressions for homovalent ion-exchange equilibrium reactions. In this sense, equilibrium constants ω_1 and ω_2 resemble the selectivity coefficients for exchange reactions and s_T resembles the exchange capacity (CEC) of soil matrix surfaces (Sposito 1981). However, a major difference between ion exchange and the proposed second-order approach is that no consideration for other competing ions in solution or matrix surfaces are incorporated in the rate of reactions. In a strict thermodynamic sense, the above equations should be expressed in terms of activities rather than concentrations. However, an implicit assumption is that solution-phase ion activity coefficients are constant in a constant ionic strength medium. Moreover, the solid phase ion activity coefficients are assumed to be incorporated in the selectivity coefficients (ω_1 and ω_2) as in ion-exchange formulations (Sposito 1981).

We now consider the case where only one type of active site is dominant in the soil system. In a fashion similar to the formulations of eq 7-9 and 7-10, the kinetics of the reaction can be generalized by the following reversible Langmuir equation:

$$\rho \frac{\partial s}{\partial t} = \Theta k_f \phi c - \rho k_b s \quad (7-11)$$

Here k_f and k_b (hr^{-1}) are the forward and backward retention rate coefficients and s is the total amount of solute retained by the soil matrix surfaces. Reaction 7-11 at equilibrium obeys the widely recognized Langmuir isotherm equation

$$s/S_T = Kc/(1+Kc), \quad (7-12)$$

where $K = (\Theta k_f / \rho k_b)$ and K is equivalent to ω of eq 7-9 and 7-10. For recent discussions on the formulation of the kinetic Langmuir equation see Rubin (1983) and Jennings and Kirkner (1984).

It should be recognized that the unfilled or vacant sites (ϕ) in eq 7-9, 7-10, and 7-11 are not really vacant. They are occupied by hydrogen, hydroxyl, or other nonspecifically (e.g., Na, Ca, chloride, nitrate) or specifically (e.g., sulfate, phosphate, transition metals) adsorbed species. The terms *vacant* or *unfilled* mean vacant or unfilled by the specific solute species of interest. The process of occupying a vacant site by a given solute species actually is one of replacement or exchange of one species for another. However, the simplifying assumption on which this model is based is that the filling of sites by a particular solute species need not consider the corresponding replacement of species already occupying the sites. The Langmuir-type approach considered here (eq 7-8 through 7-11) is a specialized case of an ion exchange formulation. This was considered in detail by Elprince and Sposito (1981). Alternatively, the competitive Langmuir approach may be used if the identities of the replaced solute species are known (Jennings and Kirkner 1984, Jennings 1987).

Transport model

Incorporating the second-order two-site reactions into the classical (convection–dispersion) transport equation yields (Selim and Amacher 1988)

$$\rho \frac{\partial s_1}{\partial t} + \rho \frac{\partial s_2}{\partial t} + \Theta \frac{\partial c}{\partial t} = \Theta D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - Q. \quad (7-13)$$

Here the term Q is a sink representing the rate of irreversible heavy metal reactions by direct removal from the soil solution ($\text{mg day}^{-1} \text{cm}^{-3}$). In this model, the sink term was expressed in terms of a first-order irreversible reaction for reductive sorption or precipitation or internal diffusion as outlined by Amacher et al. (1986, 1988):

$$Q = \Theta k_s c, \quad (7-14)$$

where k_s is the rate constant for irreversible reaction (hr^{-1}). Eq 7-14 is similar to that for diffusion-controlled precipitation reaction if one assumes that the equilibrium concentration for precipitation is negligible and that k_s is related to the diffusion coefficient (Stumm and Morgan 1981).

For convenience, we define the dimensionless variables

$$X = x/L, \quad (7-15)$$

$$T = vt/L\Theta, \quad (7-16)$$

$$C = c/C_o, \quad (7-17)$$

$$S = s/s_T, \quad (7-18)$$

$$\Phi = \phi/s_T, \quad (7-19)$$

$$P = vL/D \Theta, \quad (7-20)$$

where T is dimensionless time equivalent to the number of pore volumes leached through a soil column of length L , and P is the Peclet number (Brenner 1962). Given the above variables, eq 7-13, 7-7, and 7-8 are rewritten in dimensionless form, respectively, as (Selim and Amacher 1988)

$$\Omega [\partial S_1/\partial T + \partial S_2/\partial T] + \partial C/\partial T = (1/P) \partial^2 C/\partial X^2 - \partial C/\partial X - k_s C \quad (7-21)$$

$$\partial S_1/\partial T = \kappa_1 \Phi_1 C - \kappa_2 S_1 \quad (7-22)$$

$$\partial S_2/\partial T = \kappa_3 \Phi_2 C - \kappa_4 S_2 \quad (7-23)$$

where

$$\Omega = s_T \rho / C_o \Theta, \quad (7-24)$$

$$\kappa_s = k_s \Theta L / v, \quad (7-25)$$

$$\kappa_1 = k_1 \Theta^2 C_o L / \rho v \quad \text{and} \quad \kappa_3 = k_3 \Theta^2 C_o L / \rho v, \quad (7-26)$$

$$\kappa_2 = k_2 \Theta L / v \quad \text{and} \quad \kappa_4 = k_4 \Theta L / v. \quad (7-27)$$

Here, κ_s , κ_1 , κ_2 , κ_3 , and κ_4 are dimensionless kinetic rate coefficients that incorporate v and L . As will be shown under Transport below, these dimensionless variables (including Ω , C , S , and Φ) represent a convenient way to study the sensitivity of the model to reduced variables.

For simulation and model evaluation, the appropriate initial and boundary conditions associated with eq 7-21 through 7-23 were as follows. We chose uniform initial solute concentration C_i in a finite soil column of length L such that,

$$C = C_i \quad (T = 0, 0 < X < 1). \quad (7-28)$$

We also assume that an input solute solution pulse with a (dimensionless) concentration C_o was applied at the soil surface for a (dimensionless) time T_p and was then followed by a solute-free solution. As a result, at the soil surface the following third type boundary conditions were used (Selim and Mansell 1976, Parker and van Genuchten 1984):

$$1 = C - (1/P) \partial C/\partial X, \quad (X = 0, T < T_p) \quad (7-29)$$

$$0 = C - (1/P) \partial C/\partial X, \quad (X = 0, T > T_p) \quad (7-30)$$

and at $x = L$, we have

$$\partial C/\partial X = 0 \quad (X = 1, T > 0). \quad (7-31)$$

The differential equations of the SOTS model are of the nonlinear type, and analytical solutions are not available. Therefore, eq 7-21 through 7-23 were solved numerically using finite difference approximations (explicit-

implicit) subject to the above initial and boundary conditions. The numerical solution was compared to results obtained using a closed-form solution for linear type problems. For all cases considered, a mass balance was maintained as a check on the numerical results. Differences between calculated mass and the input for a solute pulse input were not allowed to exceed 3%. The resulting numerical scheme is documented in the SOTS model program, which is written in Fortran.

Briefly, the convection–dispersion equation and the second-order two-site retention equations were expressed in their finite difference approximation forms. Upon rearrangement and incorporation of the initial and boundary conditions (in their finite difference forms), a solution is achieved. Details of the numerical procedure and the step-by-step derivation of the solution are similar to those given in Chapter 3 for the multireaction and transport model (MRTM). The SOTS model was solved in a sequential manner where a solution is obtained for each time step until the desired time for simulation is attained.

To improve the accuracy of the approximate solution, a simple iteration scheme was incorporated in the SOTS model. The number of iterations desired must be provided by the user. No criteria are given here for the optimum number of iterations; rather a mass balance was performed (input vs output) as a check on the accuracy of the numerical solution. The user is free to adjust the number of iterations based on mass balance calculations or the convergence and stability of the numerical solution. If no iteration is desired, he may utilize the default value or specify the number of iterations to be zero in the input data section of the model.

SENSITIVITY ANALYSIS

Reaction kinetics

Several simulations were performed to illustrate the kinetic behavior of solute retention as governed by the proposed second-order reaction. We assumed a no-flow condition to describe the time-dependent batch (sorption–desorption) experiments. The problem becomes an initial-value problem where closed-form solutions are available. The retention results shown in Figure 7-1 illustrate the influence of the rate coefficients (k_1 and k_2) on the shape of the sorption isotherm (c vs s). The parameters chosen were those of a soil initially devoid of solute ($c_i = s_i = 0$ at $t = 0$) and a soil-to-solution ratio (ρ/θ) of 1:10, which is commonly used in batch experiments. Since the amount sorbed, s , was assumed to be zero initially, larger values for k_2 than k_1 were selected in our simulations to induce backward (desorption) reactions.

As shown in Figure 7-1, after 2 days of reaction, isotherm A ($k_1 = 0.01 \text{ day}^{-1}$, $k_2 = 0.1 \text{ day}^{-1}$) appears closer

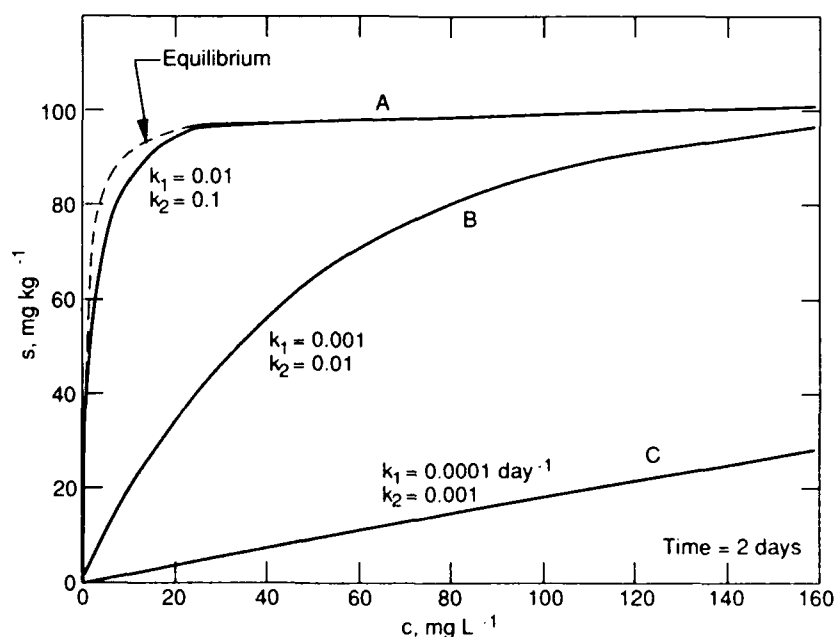
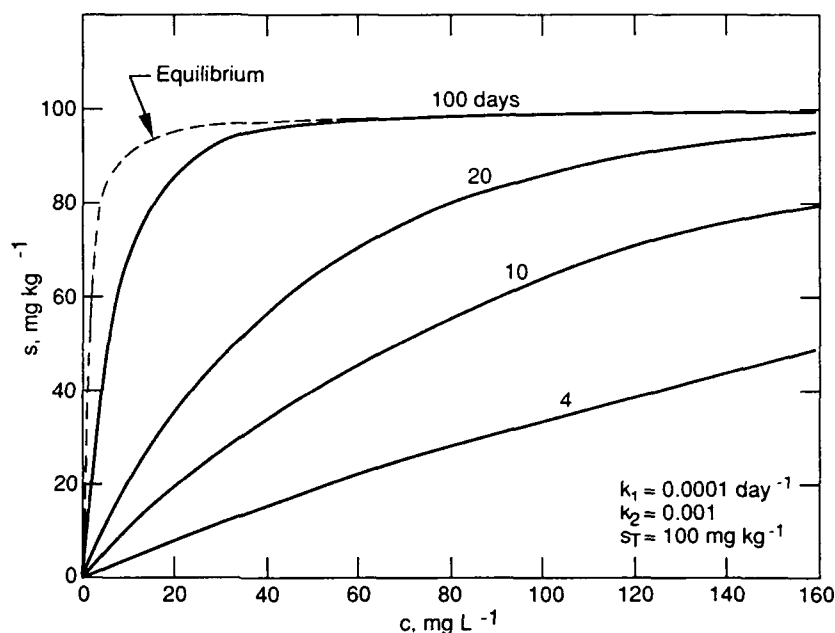


Figure 7-1. Effect of rate coefficients on sorption isotherms using the second-order kinetic model.

Figure 7-2. Effect of time of retention on sorption isotherms using the second-order kinetic model.



to the equilibrium isotherm than the other cases shown. The equilibrium case was calculated using eq 7-9 and represents an isotherm at $t \rightarrow \infty$ and/or for a soil having values of k_1 and k_2 , which are extremely large. Isotherms B and C represent cases where both k_1 and k_2 values were reduced in comparison to those for isotherm A, by one and two orders of magnitudes respectively. For both cases, the isotherms deviate a great deal from the equilibrium case. It is apparent from curve C that 2 days of reaction is insufficient, and a sorption maximum is not apparent from the shape of the isotherm. Moreover, it may be possible to consider a linear-type isotherm for the concentration range shown. However, as much as 100 days or more of reaction time is necessary to achieve closer equilibrium conditions. This is illustrated in Figure 7-2, which shows the influence of time of reaction using the second-order model.

The influence of the sorption maxima (s_T) on the retention isotherms is shown in Figure 7-3. The parameters selected were similar to those of Figure 7-2 except that a contact time of 10 days was chosen. As expected, the isotherms reached their respective maxima at lower c values with decreasing s_T . The results of Figure 7-3 also indicate a steep gradient of the retention isotherms in the low concentration range. Such a retention behavior has been observed by several scientists for a number of reactive solutes. The simulations also illustrate clearly the influence of the sorption maxima on the overall shape of the isotherms. The influence of other parameters such as F , k_3 , and k_4 on retention kinetics can be easily deduced and is thus not shown.

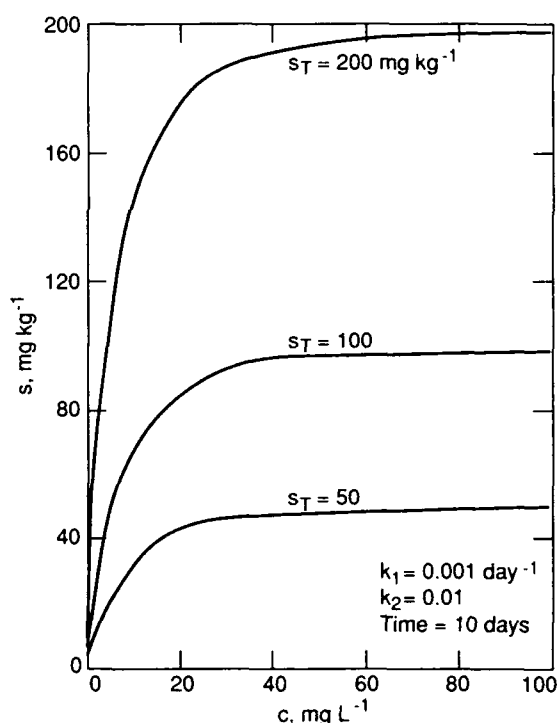


Figure 7-3. Effect of total amount of sites (s_T) on the shape of sorption isotherms using the second-order kinetic model.

Transport

Figures 7-4 through 7-6 are selected simulations that illustrate the transport of a reactive solute with the

second-order two-site (SOTS) model as the governing retention mechanism. The parameters selected for the sensitivity analysis were $\rho = 1.25 \text{ g cm}^{-3}$, $\Theta = 0.4 \text{ cm}^3 \text{ cm}^{-3}$, $L = 10 \text{ cm}$, $c_i = 0$, $c_o = 10 \text{ mg L}^{-1}$, $F = 0.50$, and $s_T = 200 \text{ mg kg}^{-1}$. Here we assumed a solute pulse was applied to a fully water-saturated soil column initially devoid of a particular heavy metal of interest. In addition, a steady water flow velocity (v) was maintained constant with a Peclet number $P (= vL/\Theta D)$ of 25. The length of the pulse was assumed to be 3 pore volumes, which was then followed by several pore volumes of a heavy-metal-free solution. The rate coefficients selected were 0.01, 0.1, 0.001, and 0.01 day^{-1} for k_1 , k_2 , k_3 , and k_4 , respectively. As a result, the equilibrium constants ω_1 and ω_2 for type 1 and 2 sites, respectively, were identical.

Figure 7-4 shows breakthrough curves (BTCs) that represent the relative effluent concentration (C/C_o) vs effluent pore volume (V/V_o) for several pulse input concentrations (C_o s). The shape of the BTCs is influenced by the input solute concentration and is due to the nonlinearity of the proposed second-order retention mechanism. The simulated results also indicate that for high C_o values the BTCs appear less retarded and have sharp gradients of the desorption (or right) side. In contrast, for low C_o values the general shape of the BTCs appears

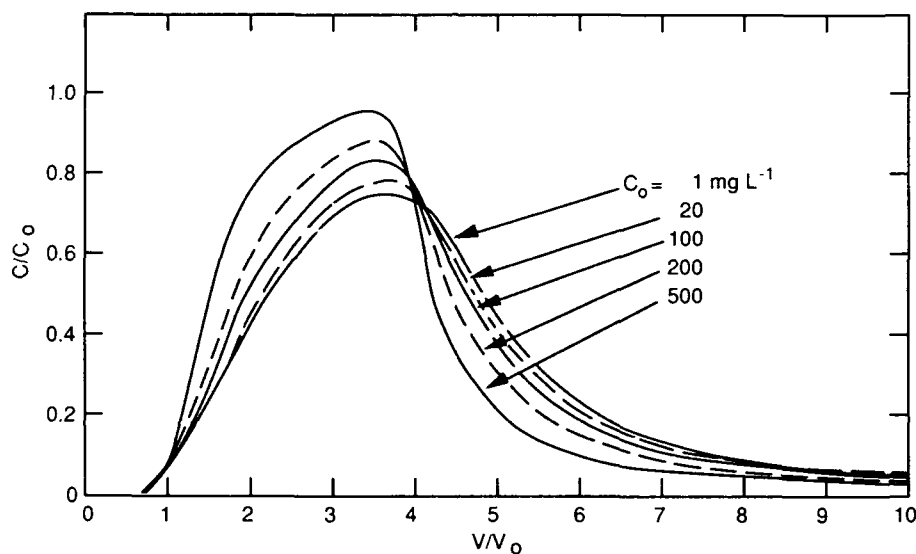


Figure 7-4. Effluent concentration distributions for different initial concentrations (C_o) using the second-order two-site (SOTS) model.

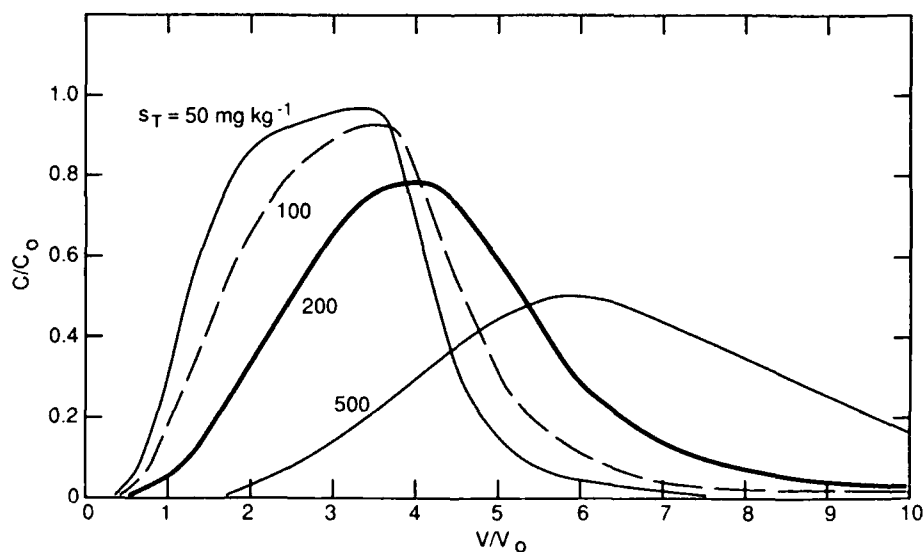


Figure 7-5. Effluent concentration distributions for different s_T values using the SOTS model.

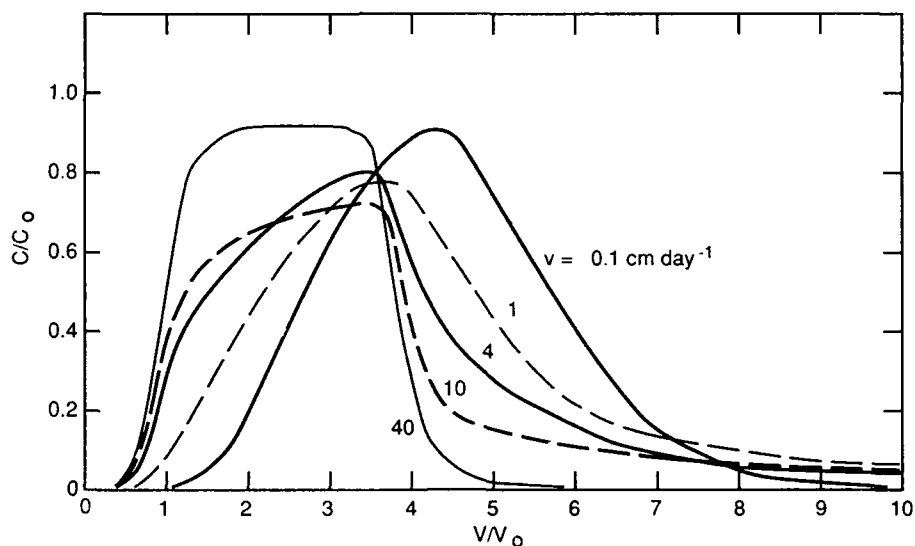


Figure 7-6. Effluent concentration distributions for different flux (v) values using the SOTS model.

to be kinetic. Specifically, as C_0 decreases, a decrease in maximum or peak concentrations and extensive tailing of the desorption side of the BTCs can be observed. The influence of the total amount of (active) sites (s_T) on the BTCs is clearly illustrated by the cases given in Figure 7-5. Here the value of C_0 was chosen constant ($C_0 = 10 \text{ mg L}^{-1}$). The BTCs show that an order of magnitude increase in s_T (from 50 to 500 mg kg^{-1}) resulted in an approximately 3-pore-volume shift in peak concentration. In addition, for high s_T values extensive tailing as well as an overall decrease of effluent concentrations (C/C_0) was observed.

The influence of the flow velocity (v) on the shape of the BTC is somewhat similar to that of the rate coefficients for retention, provided that the Peclet number remains constant. This is illustrated by the simulations shown in Figure 7-6 for a wide range of flow velocities. For $v = 40 \text{ cm day}^{-1}$, the retention reactions associated with type 1 sites were not only dominant but also closer to local equilibrium than those for type 2 sites (results not shown). This is a direct consequence of the limited solute residence time encountered when the fluid flow velocity is exceedingly high. Type 2 sites that may be considered highly kinetic were so far removed from equilibrium that only a limited amount of solute was retained from the soil solution. Under such conditions, the amount of available sites (ϕ_2) remains high and the retention capacity of the soil matrix is therefore not achieved. In fact, curve A ($v = 40 \text{ cm day}^{-1}$) describes closely a one-site retention mechanism, as indicated by the low retardation and lack of tailing of the desorption side. As the flow velocity decreases, the solute residence time increases and more time is available for the highly kinetic type 2 sites to retain solute species from the soil solution. In addition, for extremely small velocities ($v \rightarrow 0$) the BTC should indicate maximum solute retention during transport. This probably resembles the BTCs of curve E, which indicates the highest solute retardation shown. For intermediate velocities, however, the BTCs of B, C, and D indicate relatively moderate degrees of retardation as well as tailing that is indicative of kinetic retention mechanisms.

In the BTCs shown in Figures 7-4 through 7-6, the irreversible retention mechanism for heavy metal removal (via the sink term) was ignored. The influence of the irreversible kinetic reaction (e.g., precipitation) is a straightforward one, as shown in Figure 7-7. This is manifested by the lowering of solute concentration for the overall BTC for increasing values of k_s . Since a first-order reaction was assumed, the lowering of the BTC is proportional to the solution concentration.

In previous BTCs, the sensitivity of model predictions (output) of the second-order approach to selected parameters was discussed. It is convenient, however, to carry out model sensitivity using dimensionless parameters such as those defined by eq 7-15 to 7-20. Dimensionless parameters offer a distinct advantage over conventional parameters since they provide a wide range of application as well as further insight into the predictive behavior of the model. Figures 7-8 through 7-10 are simulations that illustrate the transport of a reactive solute

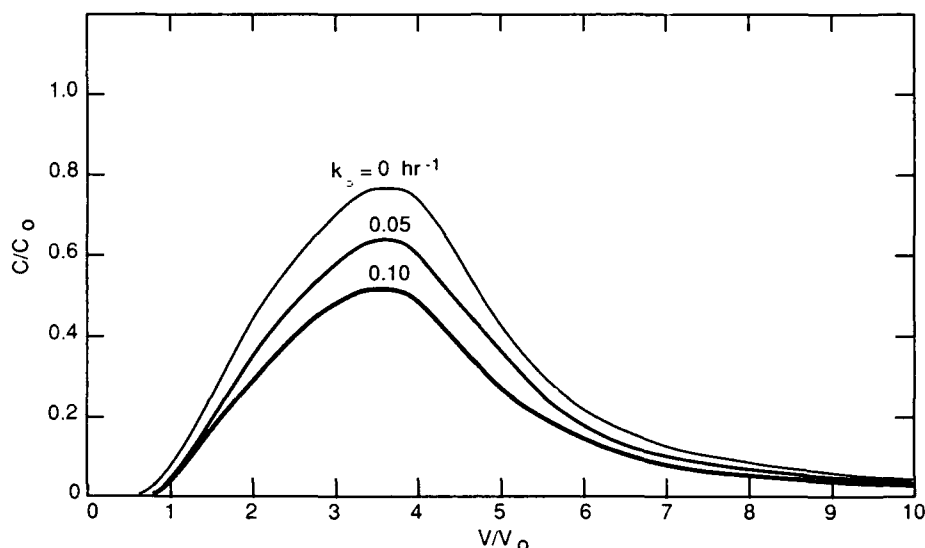


Figure 7-7. Effluent concentration distributions for values of the irreversible rate coefficient (k_s) using the SOTS model.

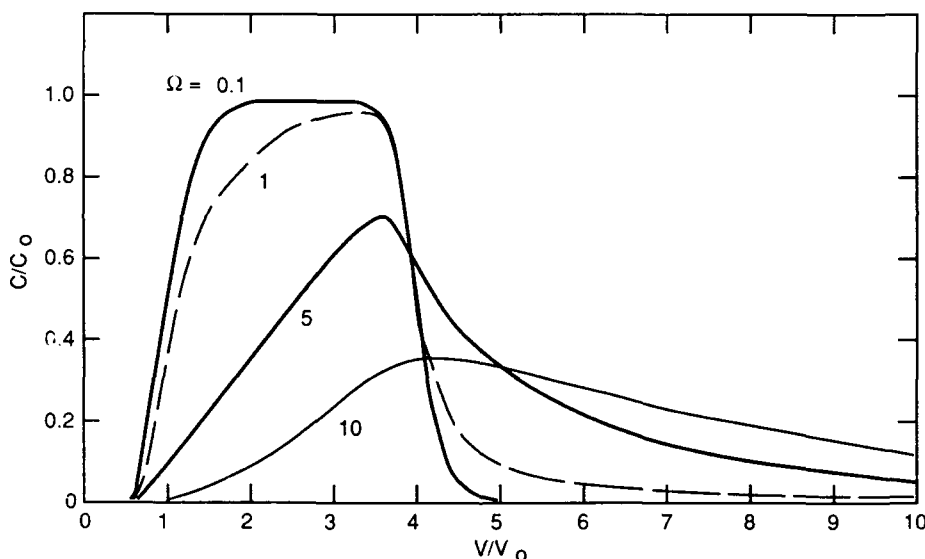


Figure 7-8. Effluent concentration distributions for different values of parameter Ω of the SOTS model.

with the SOTS model for selected dimensionless parameters. Unless otherwise indicated, the values for dimensionless parameters Ω , κ_1 , κ_2 , κ_3 , κ_4 , F , κ_s , P , and T_p were 5, 1, 1, 0.1, 0.1, 0, 0.5, 25, and 1, respectively. Figure 7-8 shows breakthrough curves (BTCs) of a reactive solute for several values of Ω . The figure indicates that the shape of the BTCs is influenced drastically by the value of Ω . This is largely due to the nonlinearity of the proposed second-order retention mechanism. As given by eq 7-24, Ω represents the ratio of total sites (S_T) to input (pulse) solute concentration (C_0). Therefore, for small Ω s (e.g., $\Omega = 0.1$), the simulated BTC is very similar to that for a nonretarded solute, due to the limited amount of sites (S_T) in comparison to C_0 . In contrast, large values of Ω resulted in BTCs that indicate increased retention as manifested by the rightward shift of the peak concentration of the BTCs. In addition, for high Ω s, extensive tailing as well as an overall decrease of effluent concentration was observed.

The effect of the dimensionless reaction rate coefficients (κ_1 , κ_2 , κ_3 , and κ_4) of the two-site model on solute

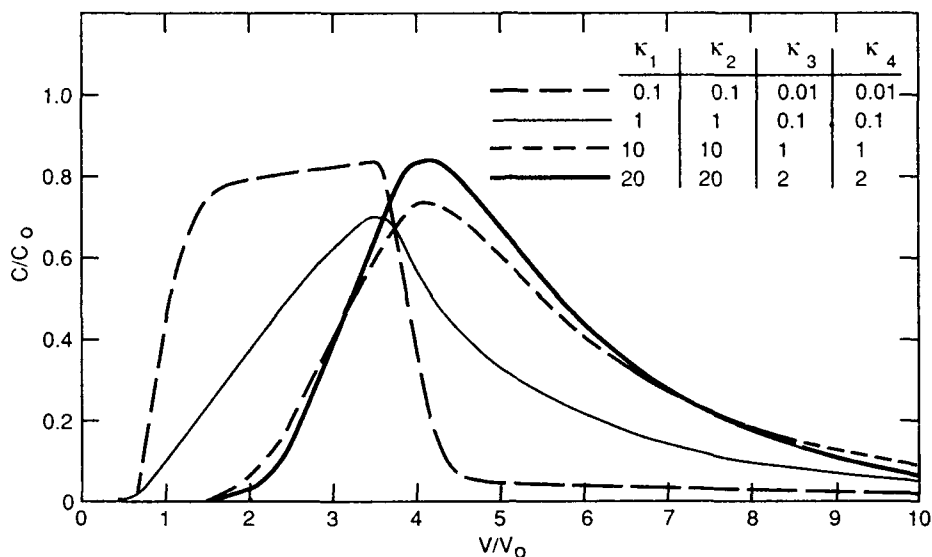


Figure 7-9. Effluent concentration distributions for different values of rate coefficients (κ_1 , κ_2 , κ_3 , and κ_4) using the SOTS model.

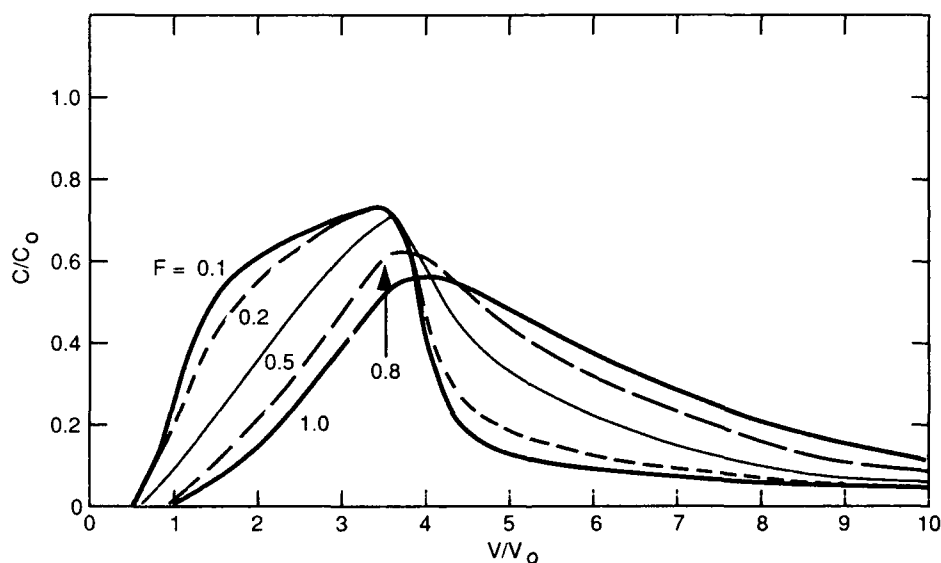


Figure 7-10. Effluent concentration distributions for different values of the fraction of sites F using the SOTS model.

retention and transport is illustrated by the BTCs of Figure 7-9 where a range of rate coefficients differing by three orders of magnitude was chosen. For the BTCs shown, the rate coefficients for type 2 sites were chosen to be one order of magnitude smaller than those associated with type 1 sites. These BTCs indicate that, depending on the values of κ_1 , κ_2 , κ_3 , and κ_4 , two extreme cases can be illustrated. For large κ values, rapid sorption-desorption reactions occurred for both type 1 and type 2 sites. Rapid reactions indicate that the retention process is less kinetic and the BTCs can approximate local equilibrium conditions in a relatively short contact time (curves C and D). In contrast, for extremely small κ values (or short residence time), little retention takes place and the shape of the BTC resembles that for a nonreactive solute (curve A). The behavior of all illustrated BTCs is consistent with those for first-order kinetic and for two-site nonlinear equilibrium-kinetic reactions. Figure 7-10 shows BTCs for several values of the fraction of sites parameter F . There are similar features between the BTCs of Figures 7-8 and 7-9 and those illustrated here. For $F = 1$, all the sites are type 1 sites, which we design-

nated earlier as those sites of strong kinetic influence due to their large values of κ_1 and κ_2 . As the contribution of type 2 sites increases (or F decreases), the shapes of the BTCs become increasingly less kinetic with significant decreases in amounts of solute retention.

SOTS COMPUTER PROGRAM

The computer code for the SOTS model is written in Fortran. Two versions are available: one is for use with mainframe computers and the other with personal computers. The input and output variables used in the SOTS model are given in Tables 7-1 and 7-2, respectively. The input data required for the SOTS model is given at the end of the code for the mainframe version. The appropriate values of model parameters must be provided by the user in the input data section before the mainframe version is run.

A listing of the Fortran code for the PC version of the SOTS model (SOTSPC) is given in Appendix C. The PC version allows the user to choose to enter the required model parameters in one of two ways: interactively through the keyboard or by providing the name of an existing file that contains the input data. An example of an input data file to be used with the PC version (SOTSPC.DAT) is included in Appendix C. The input parameters listed were used for the sensitivity analysis presented in Figure 7-8. The PC version of SOTS was compiled using a Fortran compiler, which results in an executable file (SOTSPC.EXE).

To use the compiled PC version of the SOTS model, the user need only type SOTSPC to run the program. You will then be prompted for the name and destination of an output file where all model calculations will be stored. If you choose to provide the input data interactively, you will also be prompted to enter the appropriate input parameters in the order given in the data file. For convenience, default values for soil parameters and reaction rate coefficients are included. For any parameter, the default value will be used if the user does not pro-

Table 7-1. List of input parameters required for the SOTS model.

<i>Card number</i>	<i>Column number</i>	<i>Format</i>	<i>Variable name</i>	<i>Definition</i>
I	1-80	20A4	USER	User's name or any other information (optional)
II	1-80	20A4	SOIL	Soil name or any other information (optional)
III	1-80	20A4	SOLUTE	Solute species or other information (optional)
VI	1-80	20A4	DATE	Date, experiment number, or any other information (optional)
1	51-70	E20.6	TH	Soil moisture content (Θ), $\text{cm}^3 \text{cm}^{-3}$
2	51-70	E20.6	ROU	Soil bulk density (ρ), g cm^{-3}
3	51-70	E20.6	COL	Thickness of the soil profile (L), cm
4	51-70	E20.6	WFLX	Water flux (v), cm hr^{-1}
5	51-70	E20.6	CI	Initial solute concentration in soil solution (C_i), mg L^{-1}
6	51-70	E20.6	CS	Concentration of applied solution (C_0), mg L^{-1}
7	51-70	E20.6	D	Dispersion coefficient (D), $\text{cm}^2 \text{hr}^{-1}$
8	51-70	E20.6	ST	Total sorption sites (x_T), mg kg^{-1}
9	51-70	E20.6	F	Fraction of type 1 sites to total sites (F), dimensionless
10	51-70	E20.6	K1	Forward rate coefficient for type 1 sites (k_1), hr^{-1}
11	51-70	E20.6	K2	Backward rate coefficient for type 1 sites (k_2), hr^{-1}
12	51-70	E20.6	K3	Forward rate coefficient for type 2 sites (k_3), hr^{-1}
13	51-70	E20.6	K4	Backward rate coefficient for type 2 sites (k_4), hr^{-1}
14	51-70	E20.6	KS	Irreversible rate coefficient (k_s), hr^{-1}
15	51-53	I3	IT	Number of iterations (r)
16	51-70	E20.6	TPULSE	Duration of pulse (t_p), hr
17	51-70	E20.6	TTOTAL	Total simulation, hr
18	51-70	E20.6	TPRINT	Time interval for printout, hr
19	51-70	E20.6	DX	Initial guess for the depth increment (Δx), cm
20	51-70	E20.6	DT	Initial guess for the time step (Δt), hr

Table 7-2. List of output variables used in the SOTS model.

<i>Variable</i>	<i>Definition</i>	<i>Units</i>
TIME	Simulation time	hr
V/V0	Pore volumes of effluent (V/V_0)	dimensionless
C/C0	Relative concentration in effluent solution (C/C_0)	dimensionless
X	Soil depth (x)	cm
C	Solute concentration (c)	mg L ⁻¹
KAPPA1	Rate coefficient (κ_1)	dimensionless
KAPPA2	Rate coefficient (κ_2)	dimensionless
KAPPA3	Rate coefficient (κ_3)	dimensionless
KAPPA4	Rate coefficient (κ_4)	dimensionless
OMEGA	Total sorption (Ω)	dimensionless
PE	Peclet number (P)	dimensionless
S1	Amount of solutes (s_1)	mg kg ⁻¹
S2	Amount of solutes (s_2)	mg kg ⁻¹
SC1	Amount of vacant sites (ϕ_1)	mg kg ⁻¹
SC2	Amount of vacant sites (ϕ_2)	mg kg ⁻¹
SIR	Amount of s_{irr}	mg kg ⁻¹
SINP	Total amount of applied solute (input pulse) per unit area	mg cm ⁻²
TSWATR	Total amount of solute in soil solution in soil profile	mg cm ⁻²
TS1	Total amount sorbed in kinetic phase (s_1) in soil profile	mg cm ⁻²
TS2	Total amount sorbed in kinetic phase (s_2)	mg cm ⁻²
TSIR	Total amount sorbed in irreversible phase (s_{irr})	mg cm ⁻²
TEFFL	Total amount in effluent	mg cm ⁻²
BAL	Mass balance of solute	%

vide an entry. The default values represent average values of soil properties and the rate coefficients; they were taken from Selim and Amacher (1988). A sample output using the PC version of the SOTS model for the selected input parameters given by SOTSPC.DAT is included in Appendix C.

If you make a mistake in entering an input value, we recommend that you terminate the program and run the model again by typing SOTSPC.

The computer codes for the mainframe and PC versions do not require modification to run the SOTS model. Although the Fortran code can be modified, this is discouraged unless the modifications are made by an experienced user.

The most commonly encountered modifications are made to the DIMENSION statements. As written, the program code prescribes an array size of 500 for all declared variables (c, s_1 , s_2 , etc.). This represents the number of nodal points along the soil profile N where $N = \Delta x/L$. The size of incremental step Δx also depends on the value of flux v and dispersion coefficient D , which must satisfy the stability and convergence criteria (Pinder and Gray 1977) for the numerical solution of the finite-difference form of the convection-dispersion transport equation. Upward adjustments of the array size may be necessary for large values of v or L .

Additional modifications of the computer code are only necessary if additional reactions or other changes in the model configuration must be incorporated. Otherwise, the rest of the code should not be changed.

Chapter 8. A Second-Order Mobile-Immobile Retention and Transport Model

In Chapter 7, the second-order reactions associated with type 1 and 2 sites were considered as kinetically controlled, heterogeneous, chemical retention reactions (Rubin 1983). One can assume that these processes are predominantly controlled by surface reactions of adsorption and exchange. In this sense, the SOTS model is along the same lines as the earlier two-site model of Selim et al. (1976) and Cameron and Klute (1977). Another type of two-site model is that of Villermanx (1974), which is capable of describing breakthrough curves (BTCs) from chromatography columns with two concentration maxima.

In this chapter, we invoke the second-order concept in a different manner. We consider that retention is controlled by two types of reactions: namely a chemically controlled heterogeneous reaction and a physically controlled reaction (Rubin 1983). In our analysis we will consider the chemically controlled heterogeneous reaction to be governed according to the second-order approach. In the meantime, the physically controlled reaction will be described by diffusion or mass transfer of the mobile-immobile concept (Coats and Smith 1964, van Genuchten and Wierenga 1976). To utilize this concept, we assume Θ^m ($\text{cm}^3 \text{cm}^{-3}$) as the mobile water content that is present inside large (inter-aggregate) pores where solute transport occurs by convection and dispersion. The immobile water Θ^{im} ($\text{cm}^3 \text{cm}^{-3}$) is located inside aggregate pores (intra-aggregate) where the solute transfer occurs by diffusion only. c^m and c^{im} (mg L^{-3}) are heavy metal concentrations in the mobile and immobile phases, respectively. In addition, the soil matrix is assumed to be divided into two regions or sites, namely a dynamic or easily accessible region and a less accessible region. The dynamic region is located close to the mobile water phase, while the stagnant region is in contact with the immobile phase. Additional details on the assumptions of the mobile-immobile (or two-region) approach are given in Coats and Smith (1964) and van Genuchten and Wierenga (1976). It should also be mentioned here that analogies between the mobile-immobile concept and the two-site approach can be made. One may regard the dynamic and stagnant regions for solute retention analogous to type 1 and 2 sites of the two-site concept. Nkedi-Kizza et al. (1984) presented a detailed discussion on the equivalence of the mobile-immobile and the equilibrium-kinetic two-site models.

MODEL FORMULATION

The form of the transport equation for the mobile-immobile water concept can be written as (van Genuchten and Wierenga 1976)

$$\begin{aligned} \Theta^{im} \partial c^{im} / \partial t + \rho (1 - f^m) \partial s^{im} / \partial t + \Theta^m \partial c^m / \partial t + \rho f^m \partial s^m / \partial t \\ = \Theta^m D^m \partial^2 c^m / \partial x^2 - v \partial c^m / \partial x - Q^m \end{aligned} \quad (8-1)$$

where D^m is the hydrodynamic dispersion coefficient ($\text{cm}^2 \text{hr}^{-1}$) in the mobile water region, ρ is soil bulk density (g cm^{-3}), x is distance in the soil profile (cm), and t is time (hr). The associated transfer equation governing the interaction between solute in the mobile and immobile phases is

$$\Theta^{im} \partial c^{im} / \partial t + \rho (1 - f^m) \partial s^{im} / \partial t = \alpha (c^m - c^{im}) - Q^{im}, \quad (8-2)$$

where α is the mass transfer coefficient (hr^{-1}) between the mobile and immobile phases. In addition, s^m and s^{im} (mg kg^{-1}) are the sorbed amounts in the dynamic and stagnant regions, respectively. In eq 8-1 and 8-2, the term f^m (dimensionless) denotes the fraction of dynamic or active sites to the total sites s_T (mg kg^{-1}). This term is analogous to F of the two-site model described in the previous chapter.

In this model the terms $\partial s^m / \partial t$ and $\partial s^{im} / \partial t$ represent the rates of reversible heavy metal reactions between c in soil solution and that present on matrix surfaces in the mobile (or dynamic) and the immobile regions, respectively. Moreover, irreversible reaction of heavy metals was incorporated in this model, as may be seen by

the inclusion of the sink terms Q^m and Q^{im} ($\text{mg cm}^{-3} \text{hr}^{-1}$) in eq 8-1 and 8-2, respectively. We assumed that irreversible retention or removal from solution will occur separately in the mobile and immobile water regions. However, the governing mechanism of retention for each region was assumed to follow first-order type reactions. Specifically, we propose that irreversible retention for the mobile and immobile regions be considered in our transport model as follows:

$$Q^m = \Theta^m k_s c^m \quad (8-3)$$

$$Q^{im} = \Theta^{im} k_s c^{im} \quad (8-4)$$

where k_s is the irreversible rate coefficient (hr^{-1}). The above formulations for the sink terms have not been seen elsewhere in the literature and were first proposed by Selim and Amacher (1988). Since soil matrix surfaces may behave in a separate manner to heavy metal retention, it is conceivable that the rate of irreversible reactions in the mobile region could be characteristically different from that for the immobile region. One way to achieve this is to distinguish between the rate coefficient (k_s) controlling the reaction for the two regions, e.g., k_s^m and k_s^{im} in eq 8-3 and 8-4, respectively. Such a distinction in reaction coefficients was not incorporated in our model and a single parameter k_s was thus used.

The retention mechanism associated with the mobile and immobile phases of eq 8-1 and 8-2 was considered as an equilibrium linear sorption (van Genuchten and Wierenga 1976) and was extended to the nonlinear or Freundlich type by Rao et al. (1979). Recently, multiple-ion retention expressed on the basis of ion-exchange equilibrium reactions was successfully incorporated into the mobile-immobile model (van Eijkeren and Loch 1984, Selim et al. 1987). Here, we consider reversible solute reactions to be governed by our second-order kinetic approach. Specifically, the rate of reaction for s^m and s^{im} were considered as (Selim and Amacher 1988)

$$\rho \partial s^m / \partial t = \Theta^m k_1 \phi^m c^m - \rho k_2 s^m \quad (8-5)$$

$$\rho \partial s^{im} / \partial t = \Theta^{im} k_1 \phi^{im} c^{im} - \rho k_2 s^{im} \quad (8-6)$$

where k_1 and k_2 are the forward and backward rate coefficients (hr^{-1}), respectively. Here ϕ^m and ϕ^{im} represent the vacant or unfilled sites (mg kg^{-1}) within the dynamic and the stagnant regions, respectively. In addition, the terms ϕ^m and ϕ^{im} can be expressed as

$$\phi^m = s_T^m - s^m = f^m s_T - s^m \quad (8-7)$$

$$\phi^{im} = s_T^{im} - s^{im} = (1 - f^m) s_T - s^{im} \quad (8-8)$$

where s_T , s_T^m , and s_T^{im} are the total amount of the sites in the soil matrix, total sites in the dynamic region, and the total in the less accessible region (mg kg^{-1}), respectively. These terms are related by

$$s_T = s_T^m + s_T^{im} = f^m s_T + (1 - f^m) s_T \quad (8-9)$$

The unfilled sites ϕ^m and ϕ^{im} are analogous to ϕ_1 and ϕ_2 of the second-order two-site concept described in the previous chapter. We also consider s_T , which represents the total amount of filled and unfilled sites, to remain time invariant.

An important feature of the second-order retention approach (eq 8-5 and 8-6) is that similar reaction rate coefficients (k_1 and k_2) associated with the dynamic and stagnant regions were chosen. It is assumed that the retention mechanism is equally valid for the two regions of the porous media. A similar assumption was made by van Genuchten and Wierenga (1976) for equilibrium linear and Freundlich-type reactions and by Selim et al. (1987) for selectivity coefficients for homovalent ion-exchange reactions. Specifically, as $t \rightarrow \infty$, that is, when both the dynamic (or active) sites and the sites in the stagnant region achieve local equilibrium, eq 8-5 and

8-6 yield the following expressions. For the active sites associated with the mobile region,

$$\Theta^m k_1 \phi^m c^m - \rho k_2 s^m = 0 \quad \text{as } t \rightarrow \infty \quad (8-10)$$

or

$$s^m/(\phi^m c^m) = (\Theta^m k_1/\rho k_2) = \omega_1 \quad \text{as } t \rightarrow \infty \quad (8-11)$$

and for the sites associated with the immobile region we have

$$\Theta^{im} k_1 \phi^{im} c^{im} - \rho k_2 s^{im} = 0 \quad \text{as } t \rightarrow \infty \quad (8-12)$$

or

$$s^{im}/(\phi^{im} c^{im}) = (\Theta^{im} k_1/\rho k_2) = \omega_2 \quad \text{as } t \rightarrow \infty \quad (8-13)$$

Here ω_1 and ω_2 represent equilibrium constants for the retention reactions associated with the mobile and immobile regions, respectively. The formulations of eq 8-10 through 8-13 are analogous to expressions derived for the SOTS model. In this sense, the equilibrium constants ω_1 and ω_2 resemble the Langmuir coefficients with s_T as the maximum sorption capacity (Selim and Amacher 1988). They are also analogous to the selectivity coefficients associated with ion exchange reaction reactions (Selim et al. 1987).

The dimensionless forms of eq 8-1, 8-2, 8-5, and 8-6 are

$$\begin{aligned} & \Omega(1-f^m) \partial S^m/\partial T + \Omega f^m \partial S^{im}/\partial T + (1-\mu) \partial C^m/\partial T + \mu \partial C^{im}/\partial T \\ & = (\mu/P^m) \partial^2 C^m/\partial X^2 - \partial C^m/\partial X - \mu \kappa_s C^m \end{aligned} \quad (8-14)$$

$$\partial C^{im}/\partial T + [\Omega(1-f^m)/(1-\mu)] \partial S^{im}/\partial T = (\alpha) (C^m - C^{im}) - \kappa_s C^{im} \quad (8-15)$$

$$\partial S^m/\partial T = \mu \kappa_1 \Phi^m C^m - \kappa_2 S^m \quad (8-16)$$

$$\partial S^{im}/\partial T = (1-\mu) \kappa_1 \Phi^{im} C^{im} - \kappa_2 S^{im} \quad (8-17)$$

where

$$C^m = c^m/C_o, \quad C^{im} = c^{im}/C_o, \quad (8-18)$$

$$S^m = s^m/S_T, \quad S^{im} = s^{im}/S_T, \quad \Phi^m = \phi^m/S_T, \quad \Phi^{im} = \phi^{im}/S_T, \quad (8-19)$$

$$P^m = vL/D^m\Theta, \quad (8-20)$$

$$\bar{\alpha} = \bar{\alpha}L/v(1-\mu), \quad (8-21)$$

$$\mu = \Theta^m/\Theta, \quad (8-22)$$

$$X = x/L, \quad (8-23)$$

$$T = vt/\Theta L, \quad (8-24)$$

where T is dimensionless time equivalent to the number of pore volumes leached through a soil column of length L , and P^m is the Peclet number (Brenner 1962). In addition, we have defined

$$\Omega = S_T \rho / C_o \Theta, \quad (8-25)$$

$$\kappa_s = k_s \Theta L / v, \quad (8-26)$$

$$\kappa_1 = k_1 \Theta^2 C_o L / \rho v, \quad (8-27)$$

$$\kappa_2 = k_2 \Theta L / v. \quad (8-28)$$

Here, κ_s , κ_1 , and κ_2 are dimensionless kinetic rate coefficients that incorporate v and L . In addition, the initial and boundary conditions were similar to those outlined in Chapter 7 (eq 7-28 through 7-31) and are identical to those of van Genuchten and Wierenga (1976).

Initial and boundary conditions

The corresponding initial and boundary conditions associated with the SOMIM can be expressed as

$$c^m = c^{im} = c_i \quad (t = 0, 0 < x < L) \quad (8-29)$$

$$s^m = s^{im} = s_i \quad (t = 0, 0 < x < L) \quad (8-30)$$

$$v c^m = v s^m - \Theta^m D^m c^m / \partial x \quad (x = 0, t < t_p) \quad (8-31)$$

$$0 = v c^m - \Theta^m D^m \partial c^m / \partial x \quad (x = 0, t > t_p) \quad (8-32)$$

$$\partial c^m / \partial x \quad (x = L, t < 0). \quad (8-33)$$

These conditions are similar to those described earlier for the transport of a solute pulse (input) in a uniform soil having a finite length L where a steady water flux v was maintained constant. The soil column is considered to have uniform retention properties as well as uniform ρ and Θ . We further assume that there is equilibrium between the solute present in the soil solution of the mobile water (i.e., interaggregate) phase and that present in the immobile (or intra-aggregate) phase. This necessary condition is expressed by eq 8-29 and 8-30. Uniform initial conditions were assumed along the soil column. However, the user can incorporate nonuniform distribution by providing the spatial distribution in c^m , c^{im} , s^m , and s^{im} and including them in the initial condition section of the computer code. We assume that an input heavy metal solution pulse with a concentration C_o was applied at the soil surface for time duration t_p and was then followed by a solute-free solution. As a result, at the soil surface, the third-type boundary conditions were those of eq 8-31 and 8-32. In a dimensionless form, the boundary conditions can be expressed as

$$1 = C^m - (1/P^m) \partial C^m / \partial X, \quad (X = 0, T < T_p) \quad (8-34)$$

$$0 = C^m - (1/P^m) \partial C^m / \partial X, \quad (X = 0, T > T_p) \quad (8-35)$$

and at $x = L$ we have

$$\partial C^m / \partial X = 0 \quad (X = 1, T > 0) \quad (8-36)$$

where T_p is the dimensionless time of the input pulse duration of the applied solute and represents the amount of applied pore volumes of input solution.

Numerical solutions

The differential equations associated with the second-order mobile-immobile model subject to the initial and boundary conditions described above were solved using numerical approximation. The finite-difference ex-

plicit-implicit method (Remson al. 1971, Pinder and Gray 1977) was used. Finite-difference solutions provide distributions of the dependent variables (e.g., solution and sorbed phase concentrations) at incremental distances Δx and time steps Δt as desired. In a finite difference form a variable such as C is expressed as

$$C(x,t) = C(i \Delta x, j \Delta t) \quad (8-37)$$

$$\text{where } i = 1, 2, 3, \dots, N \quad \text{and} \quad j = 1, 2, 3, \dots \quad (8-38)$$

$$x = i \Delta x, \quad \text{and} \quad t = j \Delta t \quad (8-39)$$

where N is the number of incremental distances in the soil ($N = L/\Delta x$). For simplicity, the concentration $C(x,t)$ may be abbreviated as

$$C(x,t) = C_{i,j} \quad (8-40)$$

where subscript i denotes incremental distance in the soil and superscript j denotes the time step. We assume that the concentration distribution at all incremental distances (Δx) is known for time j . We seek to obtain a numerical approximation of the concentration distribution at time $j+1, j+2$, and so on. The convection-dispersion equation along with the retention equations for reversible and irreversible reactions must first be expressed in their finite difference approximation forms. Upon rearrangement and incorporation of the initial and boundary conditions (in their finite difference forms), a solution is achieved. Details of the numerical scheme and the step-by-step derivation of the solution are provided in Chapter 3 and are similar to those of Selim and Iskandar (1980) for nitrogen transport.

The second-order mobile-immobile (SOMIM) model is solved in a sequential manner. Specifically, a solution is obtained for each time step until the desired time for simulation is attained. It should be emphasized here that the number of iterations, which are incorporated into the model to improve the accuracy of the solution at every time step, for the above calculations must be provided by the user. No criteria are given here for the optimum number of iterations, rather a mass balance was performed (input vs output) as a check on the accuracy of the numerical solution. Therefore, the user is free to adjust the number of iterations based on mass balance calculations or other criteria as desired.

SENSITIVITY ANALYSIS

Figures 8-1 through 8-5 are examples of simulated breakthrough curves (BTCs) to illustrate the sensitivity of the proposed second-order reaction, when incorporated into the mobile-immobile concept, to various model parameters. As shown, several features of the mobile-immobile concept dominate the behavior of solute transport and thus the shape of the simulated BTCs. For this reason we restrict our discussion to the influence of parameters pertaining to the proposed second-order mechanism. Specifically, the influence of k_1 and k_2 (or κ_1 and κ_2) and ω on solute retention were examined. Other parameters, such as D^m and v , have been rigorously examined in earlier studies (Coats and Smith 1964, van Genuchten and Wierenga 1976).

For the simulations shown in Figures 8-1 to 8-5, initial conditions, volume of input pulse, and model parameters were identical to those used for the SOTS model, where $c_i = s_i = 0$ within the mobile and immobile regions. Specifically, the parameters chosen were $L = 10$ cm, $D^m = 1$ cm² hr⁻¹, $\rho = 1.2$ g cm⁻³, $f^m = 0.50$, $\Theta = 0.40$ cm³ cm⁻³, $\mu = \Theta^m/\Theta = 0.5$, $c_o = 100$ mg L⁻¹, $s_T = 200$ mg hr⁻¹, and a Peclet number $P^m = 25$. Unless otherwise stated, the values selected for dimensionless parameters κ_1 , κ_2 , κ_s , Ω , and α used were 1, 1, 0.5, and 1, respectively. We assumed a solute pulse was applied to a fully water-saturated soil column initially devoid of a particular heavy metal of interest. In addition, a steady water flow velocity (v) was maintained constant with a Peclet number P of 25. The length of the pulse was assumed to be 3 pore volumes, which was then followed by several pore volumes of a heavy-metal-free solution.

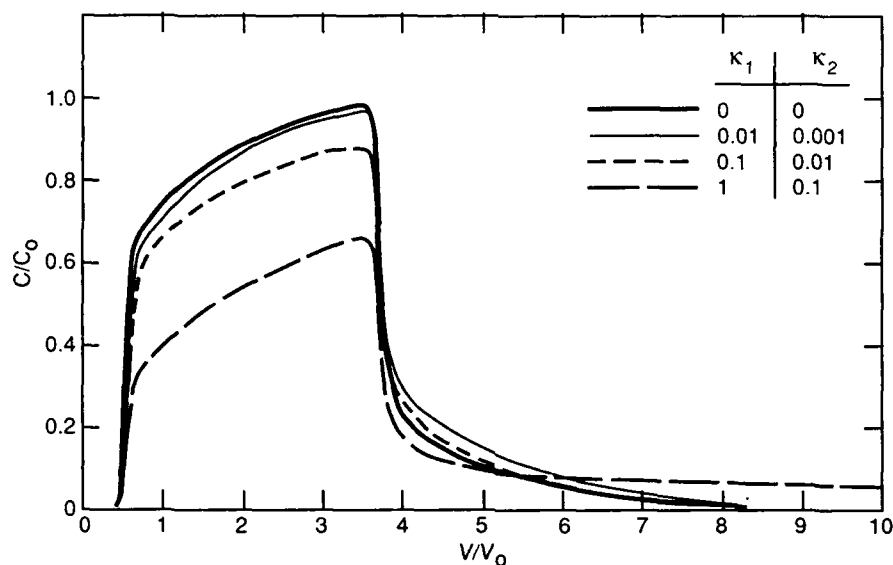


Figure 8-1. Effluent concentration distributions for different values of κ_1 and κ_2 using the SOMIM.

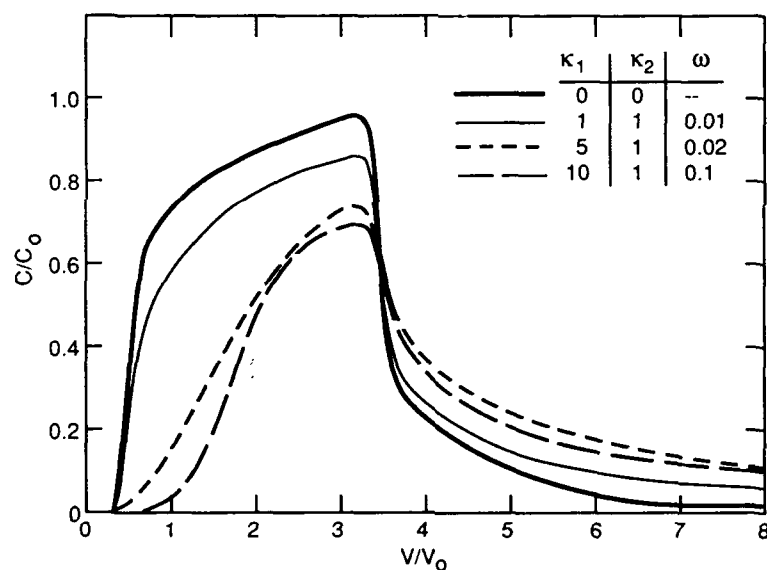


Figure 8-2. Effluent concentration distributions for different values of parameter ω using the SOMIM. Values of κ_1 and κ_2 are also shown.

The influence of the reaction rate coefficients on the shape of the BTCs is illustrated in Figure 8-1. Here the values of κ_1 and κ_2 were varied simultaneously, provided that κ_1/κ_2 (and ω_1 and ω_2) remained invariant. For the nonreactive case ($\kappa_1 = \kappa_2 = 0$), the highest effluent peak concentration and least tailing was observed. As the rate of reactions increased simultaneously, solute peak concentrations decreased and excessive tailing of the BTCs was observed. However, the arrival time or the location of peak concentration was not influenced by increasing the rates of reactions.

The effect of increasing values of equilibrium constant ω , which represents the ratio of κ_1/κ_2 (see eq 7-9b, 7-10b, 7-26, and 7-27), on the shape of the BTCs is shown in Figure 8-2. Here a constant value of 1 was chosen for κ_2 ; κ_1 was allowed to vary. For all BTCs shown in Figure 8-2, the values of ω_1 and ω_2 were equal (since $\mu = 0.5$), so we refer simply to ω rather than ω_1 and ω_2 . The results indicate that as the forward rate of reaction

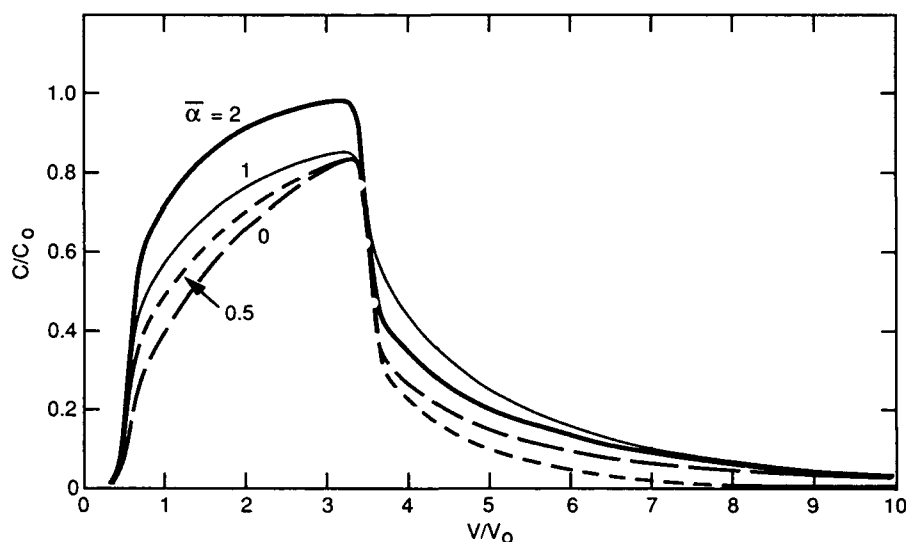


Figure 8-3. Effluent concentration distributions for different values of the dimensionless mass transfer parameter $\bar{\alpha}$ of the SOMIM.

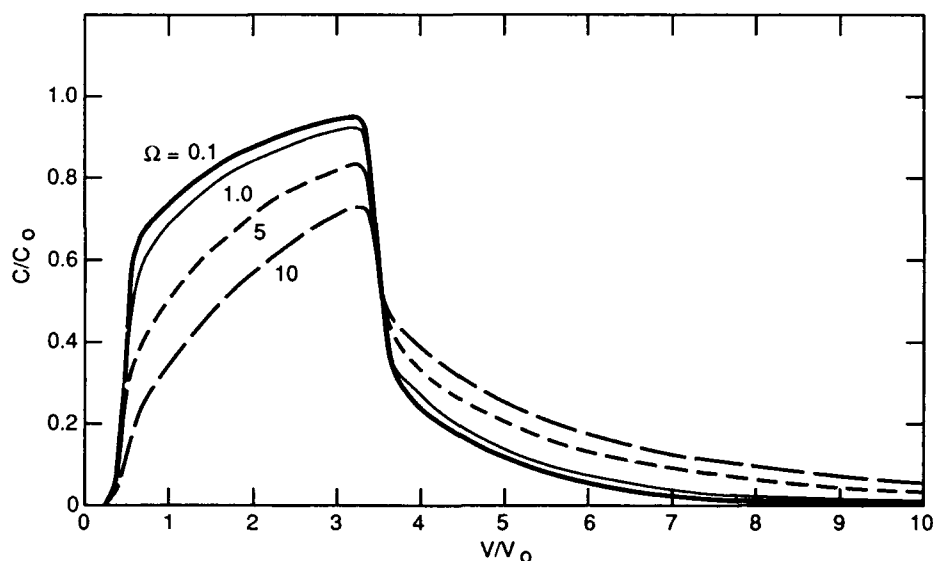


Figure 8-4. Effluent concentration distributions for different values of parameter Ω of the SOMIM.

(κ_1) increased, there was an increase in solute retardation or a rightward shift of the BTCs. This shift was accompanied by an increase in solute retention (i.e., a decrease of the amount of solute in the effluent, based on the area under the curve) and a lowering of peak concentrations. Similar behavior was observed for the influence of the dimensionless transfer coefficient ($\bar{\alpha}$) on the shape of the BTCs, as may be seen in Figure 8-3. For very large values of $\bar{\alpha}$ (>2), the diffusion between the mobile and immobile phases became more rapid. Therefore, equilibrium between the two phases is nearly attained (Valocchi 1985).

Figure 8-4 shows breakthrough curves (BTCs) of a reactive solute for several values of Ω . The figure indicates that the shape of the BTCs is influenced drastically by the value of Ω . This is largely due to the nonlinearity of the proposed second-order retention mechanism. As given by eq 8-25, Ω represents the ratio of total sites (S_T) to input (pulse) solute concentration (C_0). Therefore, for small Ω s (e.g., $\Omega = 0.1$), the simulated BTC is very similar to that for a nonretarded solute, due to the limited amount of sites (S_T) in comparison to C_0 . In contrast,

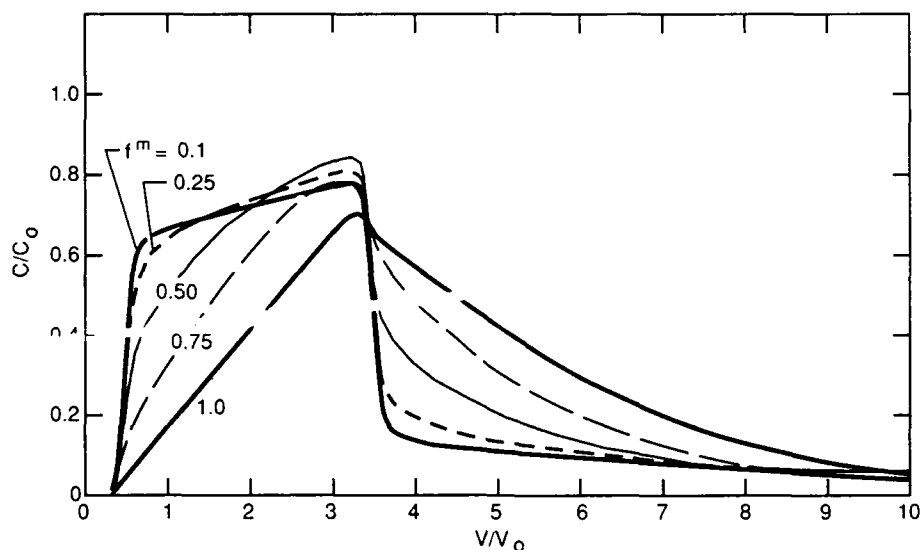


Figure 8-5. Effluent concentration distributions for different values of the fraction of active sites f^m of the SOMIM.

large values of Ω resulted in BTCs that indicate increased retention, as manifested by the right shift of peak concentration of the curves. In addition, for high Ω s, extensive tailing as well as an overall decrease in effluent concentration was observed.

The influence of parameter f^m , which represents the fraction of active or dynamic sites within the mobile region to the total amount of sites on the behavior of solute retention and transport, is shown in Figure 8-5 for several values of f^m . There are similar features between these BTCs and those illustrated in the previous figures. For $f^m = 1$, all the sites are active sites and thus there is no solute retention by the sites in the immobile region (that is, stagnant sites). As the contribution of the stagnant sites increases (or f^m decreases), the shapes of the BTCs become increasingly less kinetic with significant increase of the tailing of the desorption side of the curves.

In the BTCs shown in Figures 8-1 through 8-5 the irreversible retention mechanism for heavy metal removal (via the sink term) was ignored. The influence of the irreversible kinetic reaction (such as precipitation) is a straightforward one, so it is not shown. This is manifested by the lowering of solute concentration for the overall BTC for increasing values of k_s . Since a first-order reaction was assumed, the lowering of the BTC is proportional to the solution concentration. The influence of other parameters, such as P^m , D^m , and v , on the behavior of solute in soils with the SOMIM have been studied elsewhere (van Genuchten and Weirenga 1976, Selim and Mansell (1976) and are thus not examined here.

SOMIM COMPUTER PROGRAM

The computer code for the SOMIM is written in Fortran. It consists of a source (or main) program and two subroutines, TRIDM and INTEG. The source program outlines the DIMENSION and COMMON statements, the READ statements for the input parameters, the WRITE statements for the output data, and carries out the overall step-by-step sequence of program calculations. In addition, it calculates the time steps and incremental distances that satisfy the stability and convergence criteria (Pinder and Gray 1977) for the numerical solution for each given problem. All computations of the finite-difference approximations for the convection-dispersion equation and the retention equations and calculation of the coefficients needed for the set of equations at each iteration and for each time step are also carried out in the source program. The input and output variables used in the SOMIM are given in Tables 8-1 and 8-2, respectively.

Table 8-1. List of input parameters required for SOMIM.

Card number	Column number	Format	Variable name	Definition
I	1-80	20A4	USER	User's name or any other information (optional)
II	1-80	20A4	SOIL	Soil name or any other information (optional)
III	1-80	20A4	SOLUTE	Solute species or other information (optional)
VI	1-80	20A4	DATE	Date, experiment number, or any other information (optional)
1	51-70	E20.6	TH	Soil moisture content (Θ), $\text{cm}^3 \text{cm}^{-3}$
2	51-70	E20.6	ROU	Soil bulk density (ρ), g cm^{-3}
3	51-70	E20.6	COL	Thickness of soil profile (L), cm
4	51-70	E20.6	WFLX	Water flux (v), cm hr^{-1}
5	51-70	E20.6	CI	Initial solute concentration in soil solution (C_i), mg L^{-1}
6	51-70	E20.6	CS	Concentration of applied solute solution (C_o), mg L^{-1}
7	51-70	E20.6	D	Dispersion coefficient (D), $\text{cm}^2 \text{hr}^{-1}$
8	51-70	E20.6	ST	Total sorption sites (s_t), mg kg^{-1}
9	51-70	E20.6	F	Fraction of sites in dynamic (or active sites in mobile) region to total amount of sites (f^m), dimensionless
10	51-70	E20.6	FTH	Fraction of mobile water to total water content (Θ^m/Θ), dimensionless
11	51-70	E20.6	K1	Forward rate coefficient (k_1), hr^{-1}
12	51-70	E20.6	K2	Backward rate coefficient (k_2), hr^{-1}
13	51-70	E20.6	KS	Irreversible rate coefficient (k_i), hr^{-1}
14	51-70	E20.6	TR	Mass transfer coefficient (α), hr^{-1}
15	51-53	I3	IT	Number of iterations (r)
16	51-70	E20.6	TPULSE	Duration of pulse (t_p), hr
17	51-70	E20.6	TTOTAL	Total simulation, hr
18	51-70	E20.6	TPRINT	Time interval for printout, hr
19	51-70	E20.6	DX	Initial guess for depth increment (Δx), cm
20	51-70	E20.6	DT	Initial guess for time step (Δt), hr

Table 8-2. List of output variables used in SOMIM.

Variable	Definition	Units
TIME	Simulation time (t)	hr
V/V0	Pore volume of effluent (V/V_o)	dimensionless
C/C0	Relative concentration in effluent solution (C/C_o)	dimensionless
X	Soil depth (x)	cm
CM	Solute concentration in the mobile region (c^m)	mg L^{-1}
CIM	Solute concentration in the immobile region (c^{im})	mg L^{-1}
KAPPA1	Rate coefficient (κ_1)	dimensionless
KAPPA2	Rate coefficient (κ_2)	dimensionless
KAPPAS	Rate coefficient (κ_i)	dimensionless
TRANSC	Rate coefficient (α)	dimensionless
OMEGA	Total sorption (Ω)	dimensionless
PE	Peclet number (P)	dimensionless
SM	Amount of solutes sorbed in the active region (s^m)	mg kg^{-1}
SIM	Amount of solutes sorbed in the stagnant region (s^{im})	mg kg^{-1}
SIR	Amount of s_{ir}	mg kg^{-1}
TSMW	Total amount of solute in solution in mobile phase	mg cm^{-2}
TSIMW	Total amount of solute in solution in immobile phase	mg cm^{-2}
TSM	Total amount sorbed in active region (s^m) of soil profile	mg cm^{-2}
TSIM	Total amount sorbed in stagnant region (s^{im}) of soil profile	mg cm^{-2}
TSIR	Total amount sorbed in irreversible phase (s_{ir}) of soil profile	mg cm^{-2}
TEFFL	Total amount in effluent	mg cm^{-2}
BAL	Mass balance of solute	G

Subroutine TRIDM provides a solution for a set of linear equations using the Thomas algorithm (Pinder and Gray 1977) for tridiagonal matrix-vector equations. INTEG is an integration subroutine for equally spaced variables; it is called by the source program to calculate the mass balance (input vs output) at specified times as desired.

Two versions of the SOMIM are available: one is for use with mainframes and the other with personal computers. The input section for the mainframe version is given at the end of the Fortran code. The user must adjust the job-control cards according to the mainframe system to be utilized.

A PC version of SOMIM is provided (SOMIMPC.FOR); it requires a Fortran compiler for personal computers and includes an executable file named SOMIMPC.EXE. A computer listing of the Fortran code for the PC version is given in Appendix D. The PC version is interactive and allows the user to choose to enter the required input data in one of two ways: interactively through the keyboard, or by providing the name of an existing file that contains the input data. An example of an input data file to be used with the PC version (SOMIMPC.DAT) is included in Appendix D. The input parameters listed in SOMIMPC.DAT were used for the sensitivity analysis presented in Figure 8-2. A sample of the SOMIM output calculations for the input parameters given in SOMIMPC.DAT is included at the end of Appendix D.

To use the compiled SOMIM file, the user need only type SOMIMPC to run the program. You will then be prompted for the name and destination of an output file where all model calculations will be stored. If you choose to provide the input data interactively, you will also be prompted to enter the appropriate input parameters in the order given in the data file. For convenience, default values for soil parameters and reaction rate coefficients are included. The default value will be used for any parameter if you do not provide an entry. The default values represent average values of soil properties and the rate coefficients; they were taken from Selim and Amacher (1988).

If you make a mistake in entering an input value, we recommend that you terminate the program and run the model again by typing SOMIMPC.

The SOMIM computer codes do not require modification. Although the Fortran code can be modified, this is discouraged unless the modifications are made by an experienced user.

The most commonly encountered modifications are to the DIMENSION statements. As written, the program code prescribes an array size of 500 for all declared variables (c^m , c^{im} , s^m , etc.). This represents the number of nodal points along the soil profile N where $N = \Delta x/L$. The size of incremental step Δx also depends on the value of flux v and dispersion coefficient D , which must satisfy the stability and convergence criteria (Pinder and Gray 1977) for the numerical solution of the finite-difference form of the convection-dispersion transport equation. Adjustments of the array size may be necessary for large values of v or L . Further modifications of the computer code are only necessary if additional reactions or other changes in the model configuration must be incorporated. The remaining body of the code should not be changed.

Chapter 9. A Second-Order Retention Approach; Validation

We have presented a second-order kinetic approach for the description of solute retention during transport in soils. The basis for this approach is that it accounts for the sites on the soil matrix that are accessible for retention of the reactive solutes in solution. This approach was incorporated with the fully kinetic two-site model where the difference between the characteristics of the two types of sites is based on the rate of kinetic retention reactions. We also assume that the retention mechanisms are site-specific, e.g., the sorbed phase on type 1 sites may be characteristically different in their energy of reaction and/or the solute species from that on type 2 sites. This approach, fully described in Chapter 7, was referred to as the second-order two-site (SOTS) model. In Chapter 8, the second-order approach was extended to a diffusion-controlled mobile-immobile or two-region model (SOMIM). In the SOMIM, we assume Θ^m as the mobile water content that is present inside large (inter-aggregate) pores where solute transport occurs by convection and dispersion. The immobile water (Θ^{im}) is located inside aggregate pores (intra-aggregate) where the solute transfer occurs by diffusion only. c^m and c^{im} are solute concentrations in the mobile and immobile phases, respectively. In addition, the soil matrix is assumed to be divided into two regions (or sites), namely a dynamic or easily accessible region and a less accessible region. The dynamic region is located close to the mobile water phase, and the stagnant region is in contact with the immobile phase (for additional details see van Genuchten and Wierenga 1976). Analogies between the mobile-immobile concept and that of the two-site approach can be made. One may regard the dynamic and stagnant regions for solute retention as analogous to the type 1 and 2 sites of the two-site concept. Nkedi-Kizza et al. (1984) presented a detailed discussion on the equivalence of the mobile-immobile and the equilibrium-kinetic two-site models.

A prerequisite for the validation of a model, such as the proposed SOTS model and the SOMIM, is that the necessary (input) model parameters be obtained independently. In this chapter, model validations were carried out using batch and miscible displacement data sets for Cr(VI) from three different soils. Furthermore, whenever possible we used parameters that were either independently measured or estimated by indirect means.

EXPERIMENTAL

The soils used in this study are listed in Table 9-1 along with their taxonomic classification and selected chemical properties. The soils were air-dried and passed through a 2-mm sieve before use. The retention of Cr(VI) by the soils was studied using the batch method outlined by Amacher et al. (1986, 1988). Initial concentrations of Cr(VI) in the solutions reacted with the soils were 1, 2, 5, 10, 25, 50, 75, and 100 mg L⁻¹. Background solution composition for the Cr solutions was 0.005 M Ca(NO₃)₂. A radionuclide tracer (7.4×10^6 Bq L⁻¹ ⁵¹Cr) was added to the Cr solutions to follow the extent of the retention reactions.

The retention experiments were carried out as follows. Duplicate 4.0-g samples of each soil were added to preweighed 50-mL polypropylene centrifuge tubes. Then 40 mL of each Cr solution was added to the duplicate samples of each soil, and the samples were vortex-mixed. The tubes were placed endwise in a box on a shaker set to shake at 120 osc min⁻¹. The samples were shaken for 15 min every 2

Table 9-1. Taxonomic classification and selected chemical properties of the three soils.

Soil	Taxonomic classification	pH	Organic matter (%)	CEC (cmol+ kg ⁻¹)	Fe ₂ O ₃ (%)
Cecil	Clayey, kaolinitic, thermic Typic Hapludults	5.1	0.24	3.72	10.2
Olivier	Fine-silty, mixed, thermic Aquic Fragiudalfs	6.4	0.99	8.31	1.14
Windsor	Mixed, mesic Typic Udipsamments	5.4	0.94	1.20	2.20

hr. After 2, 5, 8, 24, 48, 72, 96, 144, 192, 240, 288, and 336 hr, the samples were centrifuged for 5 min at $1300 \times g$, 20.0 mL of supernatant were withdrawn for counting the 320 keV ^{51}Cr peak by gamma spectrometry, the pH of the supernatants was measured, and the samples were reweighed, vortex-mixed, and returned to the shaker.

Concentrations of Cr in the sample solutions were calculated from the specific activities of the initial solutions and measured activities of the sample aliquots. Correction for radionuclide decay was avoided by counting the initial solutions each time sample aliquots were counted. The amounts of Cr retained by the soils were calculated from the differences between the initial Cr concentrations in solution and the concentrations at each sampling time, with a correction for the amounts removed for counting.

The second-order two-site (SOTS) model was used to describe the retention data sets with a nonlinear, least-squares, parameter-optimization method (van Genuchten 1981). The criteria used for estimating goodness-of-fit of the model to the data were the r-square and the root mean square statistics. The extra sum of squares principle (Kinniburgh 1986) was used to determine if there were any statistically significant improvement in the fit of the model to the data by adding more parameters (i.e., a two-reaction, three-parameter version vs a three-reaction, five-parameter version). Additional details are given in Chapter 4 and are also available in Selim and Amacher (1988).

Miscible displacement experiments were also performed to evaluate the SOTS and SOMIM models. Plexiglas columns (4.4 cm in diameter \times 6.35 cm long) were uniformly packed with each soil to a given bulk density (Table 9-1). Several pore volumes of 0.005 M $\text{Ca}(\text{NO}_3)_2$ were introduced into each column at a constant flux (Table 9-1) to equilibrate the soils with the background solution. A pulse of radio-labeled 100 mg L^{-1} Cr(VI) - 0.005 M $\text{Ca}(\text{NO}_3)_2$ solution was introduced into each column at a constant flux, followed by several pore volumes of Cr-free background solution to elute the columns and obtain a complete breakthrough curve for each soil. A fraction collector was used to collect column effluent. The 320 keV ^{51}Cr tracer was counted using gamma spectrometry. To determine the dispersion coefficient (D) and the mass transfer coefficient (α), a pulse of tritium ($^3\text{H}_2\text{O}$) and chloride-36 (^{36}Cl) was applied to each column prior to the Cr(VI) pulse. Liquid scintillation spectrometry was used to count the chloride-36 and tritium radiotracers.

KINETICS

Having formulated the model to include the total amount of sites or the retention capacity (s_T) and the fraction of type 1 sites to the total amount of sites (F), some convenient method is needed to estimate their values. If the solute retention reactions with the two types of sites are reversible and reach equilibrium, then the relationship between retained solute and solute remaining in solution can be described by the following two-site Langmuir equation:

$$s/s_T = F [\omega_1 c / (1 + \omega_1 c)] + (1 - F) [\omega_2 c / (1 + \omega_2 c)] \quad (9-1)$$

where

$$s/s_T = (s_1 + s_2)/s_T \quad (9-2)$$

Here s_T represents the total retention capacity (mg kg^{-1}) or the total number of sites on matrix surfaces as time invariant. In addition, s_1 and s_2 (mg kg^{-1}) are the amounts of solute retained (or the filled sites) on type 1 and type 2 sites, respectively, and $s (= s_1 + s_2)$ is the total amount of solute retained (or the filled sites). Moreover, F represents the fraction of type 1 sites to the total amount of sites. Equation 9-1 may be derived from the kinetic second-order two-site concept, described in Chapter 7, when equilibrium conditions become dominant. As pointed out by eq 7-9 and 7-10, when equilibrium conditions ($t \rightarrow \infty$) are reached, we have

$$\Theta k_1 \phi_1 c - \rho k_2 s_1 = 0 \quad (9-3)$$

or

$$s_1 / (\phi_1 c) = (\Theta k_1 / \rho k_2) = \omega_1 \quad (9-4)$$

and for type 2 sites, we have

$$\Theta k_3 \phi_2 c - \rho k_4 s_2 = 0 \quad (9-5)$$

or

$$s_2 / (\phi_2 c) = (\Theta k_3 / \rho k_4) = \omega_2. \quad (9-6)$$

Here ω_1 and ω_2 represent equilibrium constants for the retention reactions, and ϕ_1 and ϕ_2 are the numbers of vacant sites associated with type 1 and type 2 sites, respectively. k_1 and k_2 (hr^{-1}) are the forward and backward rates of reaction for type 1 sites, while k_3 and k_4 are the coefficients for type 2 reaction sites, respectively. Θ is the soil water content ($\text{cm}^3 \text{cm}^{-3}$), and ρ is the soil bulk density (g cm^{-3}).

The two-site Langmuir equation was used to describe data for Cr(VI) retention by Cecil, Olivier, and Windsor soils after 336 hr of reaction (Fig. 9-1, Table 9-2) using the nonlinear, least-squares, parameter-optimization scheme of van Genuchten (1981). It was assumed that the reactions between Cr(VI) in solution and the two types of sites had attained equilibrium in 336 hr even though small amounts of Cr(VI) were still being retained by the soil. The continuing reaction between Cr(VI) in solution and the soil was ascribed to an irreversible reaction that is included in the model (eq 7-14). The process responsible for this irreversible reaction is discussed below. It is important to realize that only the reactions of Cr(VI) with the two types of reaction sites were assumed to attain equilibrium in 336 hr. Overall retention had not reached equilibrium because of the irreversible reaction. However, if the magnitude of the irreversible term is small, as is the case here, then reliable estimates of s_T and F can be made although the actual s_T is somewhat smaller.

The statistical results from the parameter optimization scheme indicate a close approximation of the two-site Langmuir equation to the experimental sorption isotherms (Fig. 9-1 and Table 9-2). However, a close approximation of the data does not constitute proof that two types of reaction sites actually exist (Sposito 1982). Parameter optimization merely provides a convenient method for estimating retention parameters given a pre-

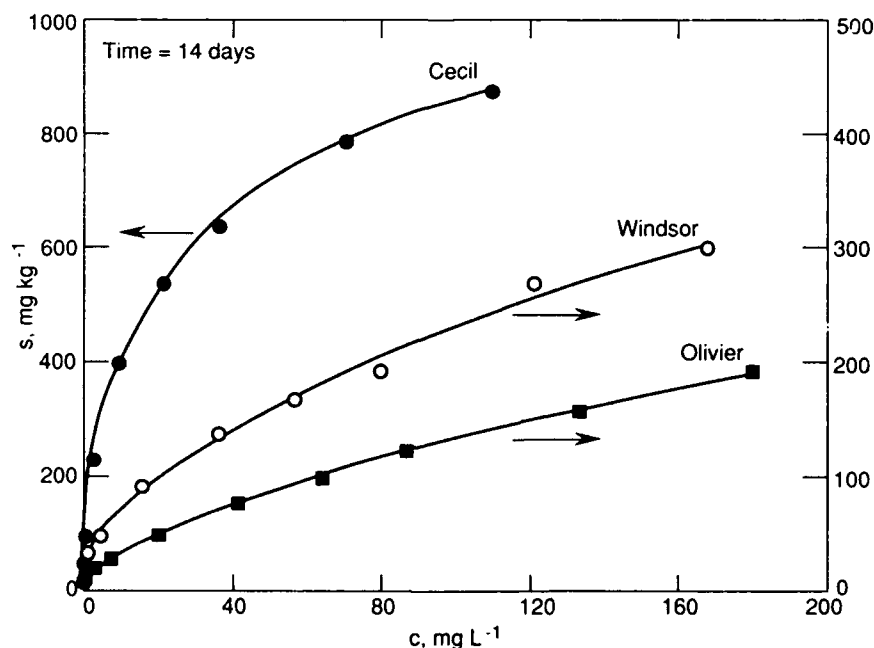


Figure 9-1. Chromium (VI) sorption isotherms for Cecil, Windsor, and Olivier soils after 14 days of reaction. The solid lines are calculated isotherms using the equilibrium two-site Langmuir model.

Table 9-2. Maximum Cr retention capacity (s_T) and fraction of sites (F) for three soils using equilibrium two-site Langmuir model.

Soil	r^2	rms	s_T (mg kg ⁻¹)	F
Cecil	0.9996	8.80	1127 ± 24	0.224 ± 0.019
Olivier	0.9997	1.56	475 ± 10	0.048 ± 0.007
Windsor	0.9983	6.11	734 ± 41	0.082 ± 0.019

site version (k_1, k_2, k_3, k_4 , and k_5) in which two types of reaction sites were considered. For most C_0 s, either the three- or five-parameter versions described the data adequately with high r -square values and low parameter standard errors. The exception was the description of retention data for Olivier soil at high C_0 where the retention of Cr(VI) was not highly kinetic and more scatter in experimental data points was observed.

For Windsor soil, the five-parameter model version provided the best description of the data at low C_0 , whereas the three-parameter model version was best for higher C_0 . A significant improvement in model goodness-of-fit was observed using the five-parameter version as compared to the three-parameter version at low C_0 values. At high C_0 no statistically significant improvement in goodness-of-fit could be obtained using the five-parameter version. Parameter values were often poorly defined with the five-parameter version at high C_0 , indicating probable overfitting of the data.

If the fraction of type 1 sites is small, as was the case with the Olivier and Windsor soils, then their contribution to the kinetic solute retention curve will be small and indistinguishable at high solute concentrations. For the Cecil soil, where the fraction of type 1 sites was significant (22.4%), the five-parameter model version was superior to the three-parameter version at all C_0 s except for $C_0 = 1 \text{ mg L}^{-1}$. Therefore, the applicability of the five-parameter version to a wide range of solute concentrations was directly related to the magnitude of the fraction of type 1 sites. As F increased (Olivier < Windsor < Cecil), the concentration range increased, over which the five-parameter version provided a better description of the data than the three-parameter version.

The shapes of the experimental data curves and model calculations (Fig. 9-2, 9-3, 9-4) are influenced by C_0 . At higher C_0 , retention of Cr(VI) from solution was far less kinetic than at lower C_0 . This behavior is as expected if the concentration of one or more reaction sites limits reaction rates. At $C_0 = 100 \text{ mg L}^{-1}$ there were 4 mg of Cr(VI) available for reaction in a 40-mL solution volume. The maximum possible amount of Cr retention in 4 g of soil was 4.5, 1.9, and 2.9 mg (solute weight basis) for Cecil, Olivier, and Windsor soils, respectively. Thus, maximum possible Cr retention in the Cecil soil was about equal to the amount of Cr available for retention, but was much less than the amount of Cr available for the Olivier and Windsor soils. Since the amount of type 1 sites was much less than the total, their contribution to the overall reaction is actually quite negligible at high solute concentrations. The influence of S_T/C_0 or Ω ($\Omega = S_T \rho / C_0 \Theta$) was defined when solute retention during transport was considered previously (see equation 7-24 and Figure 7-8).

The magnitudes of the rate coefficients in Tables 9-3, 9-4, and 9-5 also depend on C_0 , especially k_5 which decreases as C_0 increases. Although the model is successful in describing retention data for a given C_0 , the same rate coefficients cannot be used at substantially different C_0 . It is doubtful that ionic strength differences are responsible, since ionic strength varied only from 0.015 to 0.018. Differences in pH are also not likely to be responsible, since measured pH differences for all C_0 s and at all reaction times were less than a 0.3 pH unit. The variation in rate coefficients with C_0 might be attributed to changes in reaction mechanisms as C_0 increased or to failure to account for reaction components. Thus, the SOTS model may not provide a complete description of all possible processes that occur during retention. The model is capable of describing the time-dependence of solute in solution, vacant sites, and solute-site complexes. However, only removal of Cr(VI) from soil solution was experimentally measured. For a complete kinetic rate law, the time-dependence of other reaction components must also be considered such as the species already on the retention sites that were replaced by Cr ions. Thus, this model may be regarded as an apparent rate law, rather than a mechanistic one.

Although the SOTS model can accurately describe experimental data, this does not mean that it is the correct

described model. To our knowledge no reliable and independent experimental method has been developed by which the two types of reaction sites can be distinguished unambiguously and their concentrations accurately measured in soils.

The time-dependent retention of Cr(VI) by Cecil, Olivier, and Windsor soils was described using the SOTS model (Tables 9-3, 9-4, 9-5; Figures 9-2, 9-3, 9-4). Two versions of the model were used: a three-parameter or one-site version (k_1, k_2 , and k_3), in which s_T was not differentiated into type 1 and type 2 sites ($F = 1$), and a five-parameter or two-

Table 9-3. SOTS model parameters for Cr(VI) retention by Cecil soil at several initial concentrations (C_0).

C_0 (mg L ⁻¹)	No. of parameters	r^2	rms ^a	k_1	k_2 (hr ⁻¹)	k_3	k_4	k_5
1	3	0.983	0.00179	0.0128 ± 0.00101	0.0391 ± 0.00816	—	—	0.322 ± 0.086
	5	0.992	0.00118	ns ^b 0.0175 ± 0.00288	0.102 ± 0.0236	0.0127 ± 0.00388	0.0243 ± 0.00537	0.265 ± 0.0716
2	3	0.893	0.00686	0.0153 ± 0.00184	0.0387 ± 0.0126	—	—	0.155 ± 0.0900
	5	0.978	0.00310	** 0.0396 ± 0.00575	0.094 ± 0.0168	0.0113 ± 0.00111	0.0150 ± 0.00525	0.0530 ± 0.0891
5	3	0.923	0.0251	0.0130 ± 0.00122	0.0504 ± 0.0130	—	—	0.0669 ± 0.0371
	5	0.983	0.0117	** 0.0240 ± 0.00597	0.225 ± 0.0573	0.0128 ± 0.000719	0.0313 ± 0.00582	0.0395 ± 0.0253
10	3	0.971	0.0548	0.0102 ± 0.000674	0.0554 ± 0.0104	—	—	0.0345 ± 0.0172
	5	0.994	0.0250	** 0.0222 ± 0.00219	0.142 ± 0.0231	0.00797 ± 0.000339	0.0319 ± 0.00460	0.0199 ± 0.0113
25	3	0.952	0.314	0.00774 ± 0.000912	0.103 ± 0.0225	—	—	0.0133 ± 0.00583
	5	0.994	0.109	** 0.0309 ± 0.00500	0.250 ± 0.464	0.00431 ± 0.000273	0.0530 ± 0.0732	0.00872 ± 0.00267
50	3	0.967	0.830	0.00431 ± 0.000607	0.111 ± 0.0249	—	—	0.00347 ± 0.00155
	5	0.995	0.273	** 0.0214 ± 0.00565	0.294 ± 0.0820	0.00247 ± 0.000153	0.0581 ± 0.00736	0.00249 ± 0.000613
75	3	0.945	1.07	0.00555 ± 0.000937	0.198 ± 0.0429	—	—	0.00178 ± 0.000641
	5	0.994	0.345	** 0.00180 ± 0.000270	0.0338 ± 0.00652	0.00844 ± 0.000863	0.317 ± 0.0374	0.00123 ± 0.000194
100	3	0.925	1.93	0.00344 ± 0.000730	0.148 ± 0.0427	—	—	0.000940 ± 0.000563
	5	0.976	1.12	* 0.036 ± 0.145	0.374 ± 1.60	0.00193 ± 0.000305	0.107 ± 0.0246	0.000676 ± 0.000332

a = root mean square.

b = * and ** indicate that the rms for the three- and five-parameter models are significantly different at the 0.05 and 0.01 levels of probability, respectively; ns = not significant.

Table 9-4. SOTS model parameters for Cr(VI) retention by Olivier soil at several initial concentrations (C_0).

C_0 (mg L ⁻¹)	No. of parameters	r^2	rms ^a	k_1	k_2 (hr ⁻¹)	k_3	k_4	k_5
1	3	0.921	0.0344	0.00113 ± 0.000472	0.119 ± 0.0612	—	—	0.00103 ± 0.000567
2	3	0.805	0.0803	0.00155 ± 0.000915	0.194 ± 0.138	—	—	0.000789 ± 0.000566
5	3	0.889	0.130	0.00154 ± 0.000959	0.326 ± 0.232	—	—	0.000777 ± 0.000780
10	3	0.867	0.209	0.00210 ± 0.00153	0.569 ± 0.483	—	—	0.00055 ± 0.000192
25	3	0.406	1.09	0.00141 ± 0.00189	0.470 ± 0.689	—	—	0.000335 ± 0.000391
50	3	0.389	1.98	0.000441 ± 0.000645	0.155 ± 0.259	—	—	0.000101 ± 0.000366
75	3	0.272	2.15	0.000941 ± 0.000144	0.410 ± 0.594	—	—	0.000124 ± 0.000233
100	3	0.121	3.20	0.000839 ± 0.00183	0.353 ± 0.822	—	—	0.000012 ± 0.000253

a = root mean square.

Table 9-5. SOTS model parameters for Cr(VI) retention by Windsor soil at several initial concentrations (C_0).

C_0 (mg L ⁻¹)	No. of parameters	r^2	rms ^a	k_1	k_2	k_3 (hr ⁻¹)	k_4	k_5
1	3	0.969	0.208	* ^b 0.00119 ± 0.00170	0.0409 ± 0.054	—	—	0.0255 ± 0.120
	5	0.997	0.00694	0.0546 ± 0.00640	0.400 ± 0.0546	0.000502 ± 0.000079	0.0411 ± 0.00933	0.00373 ± 0.000454
2	3	0.974	0.489	0.00103 ± 0.00197	0.0437 ± 0.0593	—	—	0.0195 ± 0.138
	5	0.997	0.0144	* 0.0450 ± 0.0136	0.725 ± 0.236	0.00109 ± 0.000112	0.0883 ± 0.0122	0.00298 ± 0.000280
5	3	0.948	0.131	0.00257 ± 0.000767	0.245 ± 0.902	—	—	0.00217 ± 0.000502
	5	0.992	0.0503	* 0.00312 ± 0.000826	0.0384 ± 0.0116	0.00448 ± 0.00134	0.654 ± 0.216	0.00171 ± 0.000205
10	3	0.973	0.152	0.00173 ± 0.000351	0.219 ± 0.0559	—	—	0.00103 ± 0.000263
	5	0.993	0.0745	* 0.0114 ± 0.00135	0.0835 ± 0.0115	0.0343 ± 0.00393	116.9 ± 0.59	0.000844 ± 0.000106
25	3	0.966	0.309	0.00138 ± 0.000335	0.283 ± 0.0809	—	—	0.000524 ± 0.000153
	5	0.981	0.225	ns 0.00312 ± 0.00109	0.0639 ± 0.0254	0.00184 ± 0.000805	0.628 ± 0.300	0.000550 ± 0.000097
50	3	0.810	1.12	0.00100 ± 0.000555	0.28 ± 0.181	—	—	0.000369 ± 0.000237
75	3	0.819	1.37	0.000816 ± 0.000400	0.267 ± 0.152	—	—	0.000278 ± 0.000181
100	3	0.713	1.85	0.000648 ± 0.000375	0.229 ± 0.157	—	—	0.000133 ± 0.000175

a = root mean square.

b = * indicates that the rms for the five-parameter models is significantly different at the 0.01 level of probability; ns = not significant.

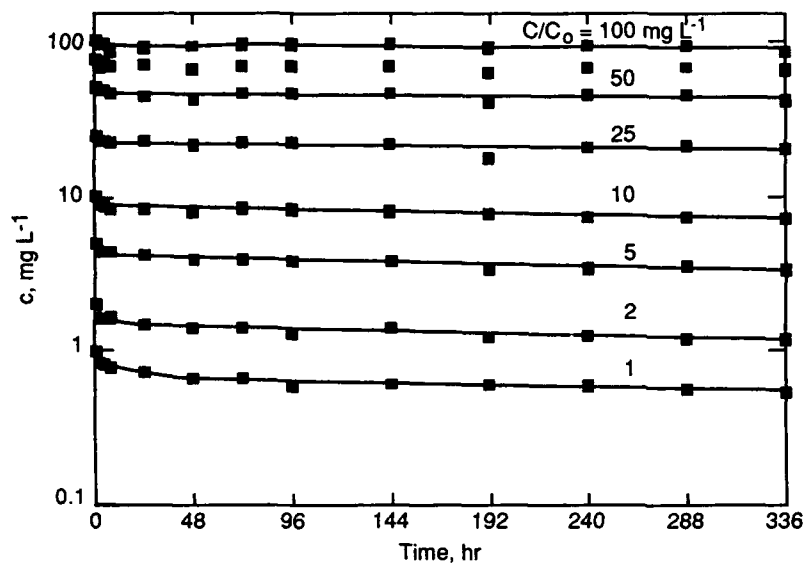


Figure 9-2. Concentration of Cr vs time for a range of initial concentrations (C_0) for Olivier soil. The solid lines are calculations using the SOTS model.

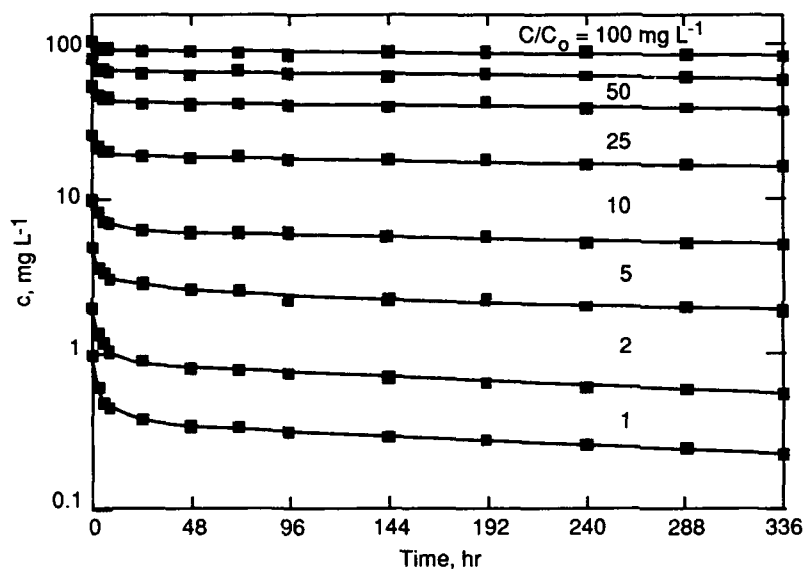


Figure 9-3. Concentration of Cr vs time for a range of initial concentrations (C_0) for Windsor soil. The solid lines are calculations using the SOTS model.

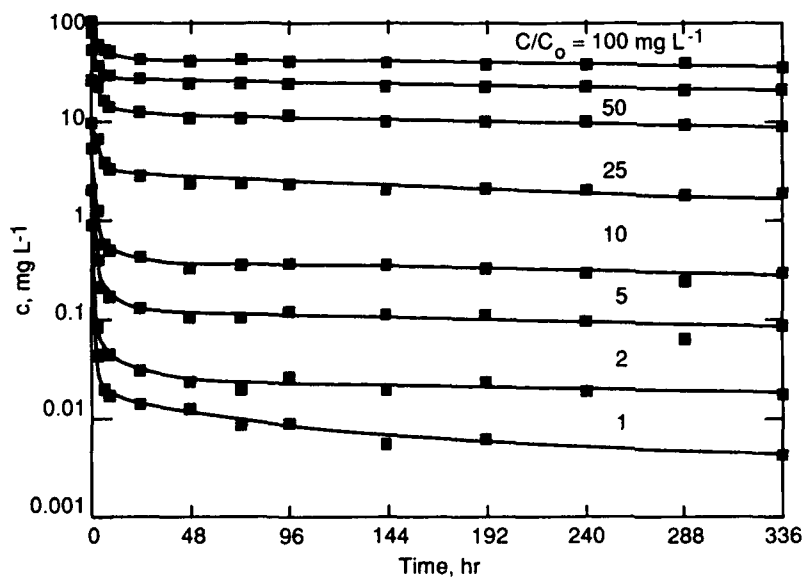


Figure 9-4. Concentration of Cr vs time for a range of initial concentrations (C_0) for Cecil soil. The solid lines are calculations using the SOTS model.

or only explanation of the data. The model does not depend on any particular process of solute retention. Any or all may be operative, including physical adsorption, formation of outer- or inner-sphere surface complexes, ion exchange, surface precipitation, etc. Furthermore, subsequent solute transformations on the soil surface or internal diffusion into soil particles may occur. Alternative processes may produce the same experimental observations and many models may give similar results. This point was thoroughly discussed by Skopp (1986) in his review of time-dependent processes in soils. Amacher and Selim (1987) and Amacher et al. (1988) found that a nonlinear multireaction model that does not include concentrations of reaction sites in its formulation can describe the experimental data as well as the SOTS model. Like the SOTS model, the nonlinear model is an incomplete description of the actual reactions because the rate coefficients are dependent on C_0 . Thus, both types of models yield pseudo rate coefficients.

Physical and chemical processes that comprise reaction mechanisms occur at the molecular level, while experimental observations on soil systems are nearly always at the macroscopic level. Identification of chemical species and reaction sites is necessary to distinguish among various possibilities, and such independent experimental evidence is for the most part lacking in the case of reactions at soil surfaces. Greater progress has been made in studying reactions at mineral surfaces (Davis and Hayes 1986). Sposito (1986) indicated that when multiple retention mechanisms operate from the beginning of contact between solute and surface, as will likely be the case in complex systems such as soils, then the time development of the overall retention process should reflect this multiplicity of processes and defy simple interpretations based on simple models or mechanisms.

The pseudo rate coefficients reported here were obtained by parameter optimization because it is not yet feasible to separate completely the reactions and determine their rate coefficients independently of each other in systems as complex as soils. Furthermore, no simple single reaction model was found to describe adequately the time-dependent data (Amacher et al. 1986). If a multireaction model does not adequately describe the data it can be discarded, but even if it does describe the data it has limited predictive and explanatory capability until independent supportive or contradictory evidence can be obtained. Despite these difficulties some limited mechanistic interpretation of the model's description of the data can be given. The retention of solute by the various types of reaction sites is postulated to be formation of outer-sphere and inner-sphere surface complexes. Such possible surface reactions are known to occur and further discussion can be found in Davis and Hayes (1986) and Sposito (1984) among other references.

Inclusion of an irreversible reaction in the model is strongly supported by the continuing reaction between Cr(VI) and the soils even after 336 hr, by the fact that overall retention was only partly reversible, and by the fact that little retained Cr could be replaced by phosphate ions (Amacher et al. 1986). A first-order irreversible reaction was chosen because at longer times and for a given C_0 , retention of Cr(VI) appeared to follow first-order kinetics. The process responsible for this irreversible reaction is postulated to be reduction of Cr(VI) to Cr(III) with possible precipitation of Cr(III) on mineral surfaces or as discrete particles of hydrous Cr(III) oxides. Organic matter, Fe(II) minerals, and other possible reducing agents are known to irreversibly reduce Cr(VI) to Cr(III). Reduction of Cr(VI) to Cr(III) by organic matter is a slow process at normal environmental pH and temperature levels such as those used in this study (Bartlett and Kimble 1976; Bartlett and James 1979; Amacher and Baker 1982; James and Bartlett 1983a,b,c) and follows first-order kinetics if pH is constant (Amacher and Baker 1982). The overall reaction rate is pH-dependent (Amacher and Baker 1982). The irreversible term in the model (eq 7-14) is fully consistent with these observations. Since k_3 is dependent on C_0 , the irreversible reaction is more complex than a simple first-order reaction. At higher C_0 , amounts of reducing agents may be limiting and thus produce the observed dependence of k_3 on C_0 . Thus, at a given C_0 the reduction reaction is pseudo first-order.

Mendoza and Barrow (1987) proposed that the continuing reaction between phosphate ions and soils is the penetration of adsorbed phosphate into the adsorbing surface. Aringhieri et al. (1985) proposed an internal diffusion process to explain why a single second-order reversible reaction failed to describe Cu and Cd retention kinetics. As an alternative to the reductive sorption mechanism, this internal diffusion mechanism may also account for part of the continuing reaction between Cr(VI) and soils. Diffusion of Cr(VI) ions into soil particles may partly explain why Cr(VI) retention is only partly reversible and retained Cr cannot be fully replaced by phosphate ions. The internal diffusion process can be accounted for by the irreversible term in the model.

SOTS MODEL VALIDATION

Chromium BTCs from the miscible displacement experiments for all three soils are shown in Figure 9-5. For Cecil and Windsor soils the measured BTCs appear to be highly kinetic, with extensive tailing. For Olivier soil little tailing was observed and approximately 100% of the applied Cr(VI) pulse was recovered. These results are consistent with the batch data, where k_s was found to be quite small.

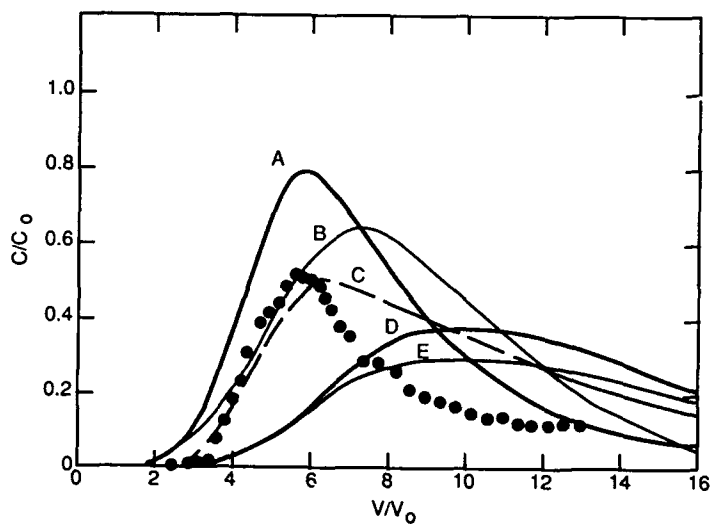
To examine the capability of the second-order two-site (SOTS) model, the necessary model parameters must be provided. In this study we will attempt to utilize, whenever possible, parameters that are either independently measured or estimated by indirect means. We will rely on parameter estimates from the batch studies discussed above for the kinetic rate coefficients, fraction of sites, and total amount of retention sites for each soil. These batch parameters were used in conjunction with the SOTS model to describe the Cr(VI) BTCs shown in Figure 9-5.

Values for the dispersion coefficients (D) were obtained from BTCs of the tracer data for tritium ($^3\text{H}_2\text{O}$) and chloride-36 (^{36}Cl) (see Table 9-6). These BTCs (figures not shown) were interpreted by use of the classical convective-dispersive equation with a retardation factor R ($R = 1 + \rho K_d / \Theta$) where K_d is the Freundlich distribution coefficient ($\text{cm}^3 \text{g}^{-1}$). Best-fit model parameters for D (and R) were obtained by use of the nonlinear least-squares optimization method of van Genuchten (1981). It should be noted here that R values for the two tracers and all three soils ranged from 0.93 to 1.07, and little tailing of the BTCs was observed. Other model parameters such as ρ , Θ , and v for each soil column are also given in Table 9-6. In addition, the values for s_T and F used to describe Cr BTCs from the SOTS model were those obtained using batch data of the sorption isotherms shown in Figure 9-2 (see Table 9-1). Direct measurements of these parameters by other than parameter optimization techniques is not available. Moreover, we utilized the reaction rate coefficients k_1 , k_2 , k_3 , k_4 , and k_s (Tables 9-3, 9-4, and 9-5) as obtained from the batch kinetic data in the predictions of Cr BTCs. In the following discussion, predicted curves imply the use of independently measured parameters in model calculations as was carried out here using the batch parameters.

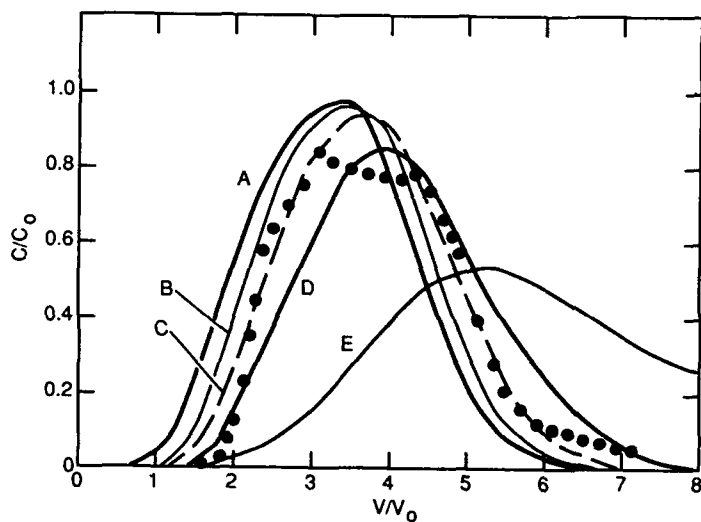
The predicted BTCs shown in Figure 9-5 were obtained using different sets of parameter values for the rate coefficients (k_1 , k_2 , k_3 , k_4 , and k_s) for the SOTS model. This is because no single or unique set of values for these rate coefficients was obtained from the batch data; rather a strong dependence of rate coefficients on input concentration was observed (see Tables 9-3 through 9-5). For all the soils, several features of the predicted BTCs are similar and indicate strong dependence on the set of rate coefficients used in model calculations. Increased sorption during transport, lowering of peak concentrations, and increased tailing were predicted when batch rate coefficients from low initial concentrations (C_0) were used.

The use of batch rate coefficients at $C_0 = 100 \text{ mg L}^{-1}$ (which is the concentration of Cr pulse inputs) grossly underestimated Cr retention by the predicted BTCs for all soils (Figure 9-5). Reasons for this failure, which has been observed by other scientists, are not fully understood. The most likely explanation is that the model is an apparent rather than mechanistic rate law as previously discussed because it may not completely account for all reactions and reaction components. Rate coefficients based on batch experiments varied with C_0 , which would be expected of pseudo rate coefficients. Unless the concentrations of unaccounted-for reaction components remain relatively constant over the course of the experiment, rate coefficients will vary with C_0 because they implicitly include concentrations of other reaction components. Much larger changes were observed in Cr concentrations in column effluent (pulse input) than in the batch solutions. Although k_1 , k_2 , k_3 , and k_4 were constant over a limited concentration range in the batch experiment, they did vary over a wide concentration range. Thus, a valid set of rate coefficients from the batch experiment is not readily available to cover the range of concentrations found in the miscible displacement experiment because of the concentration dependence of the rate coefficients. This is particularly true for k_s , which varied systematically with C_0 . Criteria for choosing rate coefficients are needed in such cases.

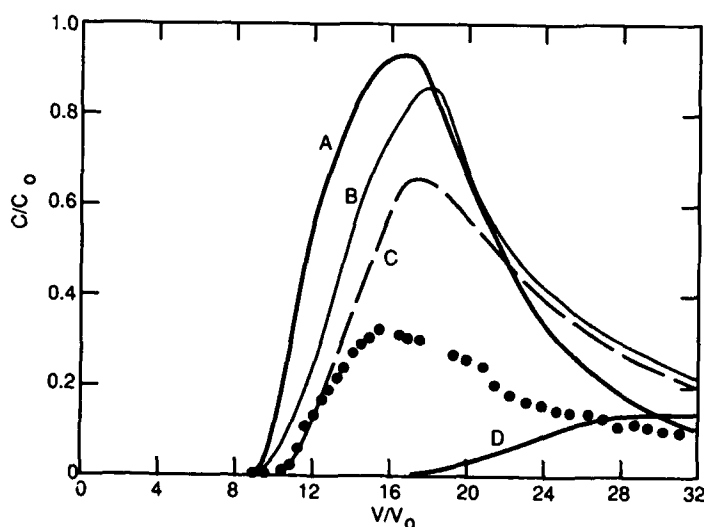
For Olivier soil, predicted BTCs using the SOTS model indicate that the batch rate coefficients from a C_0 of either 10 or 25 mg L^{-1} provided surprisingly good overall descriptions of the experimental results. Less than adequate predictions were obtained for the highly kinetic Cecil and Windsor soils, however. In fact, no one set of batch rate coefficients successfully described both the effluent and the desorption sides of Windsor or Cecil



a. Olivier soil. C/C_0 of curves A-E are 100, 25, 10, 5, and 1 mg L^{-1} , respectively.



b. Windsor soil. C/C_0 of curves A-E are 25, 10, 5, 2, and 1 mg L^{-1} , respectively.



c. Cecil soil. C/C_0 of curves A-D are 100, 50, 25, and 10 mg L^{-1} , respectively.

Figure 9-5. Effluent concentration distributions for Cr predicted using the SOTS model with the batch rate coefficients indicated.

Table 9-6. Soil physical parameters for Cr miscible displacement experiments used with the SOTS model and the SOMIM.

Parameter	Olivier	Windsor	Cecil
ρ (g cm ⁻³)	1.27	1.65	1.08
Θ (cm ³ cm ⁻³)	0.520	0.377	0.590
v (cm hr ⁻¹)	0.14	0.17	0.13
D (cm ² hr ⁻¹) (from Cl-36)	0.054	0.297	0.172
D (cm ² hr ⁻¹) (from tritium)	0.077	0.186	0.173
D^m (cm ² hr ⁻¹)	0.039	0.208	0.151
α (hr ⁻¹)	0.0758	0.0407	0.0271
Θ^m/Θ	0.73	0.80	0.66

BTCs. For both soils, closest predictions were realized using batch rate coefficients from C_0 of 10 or 25 mg L⁻¹. This finding is similar to that based on the predictions for Olivier soil.

SOMIM VALIDATION

The capability of the second-order mobile-immobile model (SOMIM) to describe Cr miscible displacement results was also examined; the predictions are shown in Figure 9-6. To obtain the predicted BTCs shown, several assumptions were necessary to estimate the model parameters. A list of parameters used in conjunction with the SOMIM are given in Table 9-6. Values for s_T were those determined from the sorption isotherms of Figure 9-1 and Table 9-2. The ratio of mobile to total

water content (Θ^m/Θ) for each soil was estimated based on soil-moisture retention relations for each soil (results not shown). We also assumed that the fraction of sites f^m is the same as the relative amount of water in the two regions, i.e., $f^m = \Theta^m/\Theta$. Such an assumption was made because independent measurement of f^m is not available (van Genuchten and Dalton 1986). Selim et al. (1987) successfully used such estimates of f^m for a well-aggregated soil. Estimates for α were obtained using

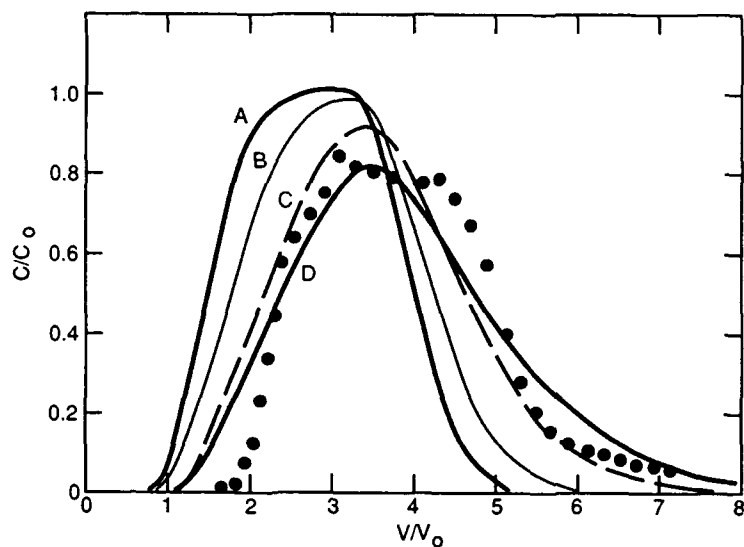
$$\alpha = 15 D^a \Theta(1-\mu)/a^2 \quad (9-7)$$

where $\mu = \Theta^m/\Theta$ and D^a is the molecular diffusion coefficient in a soil consisting of uniform aggregates of radius a . The above equation was derived by Parker and Valocchi (1986) and is based on time-moment analysis for spherical diffusion and for first-order kinetic (mobile-immobile) models. Our estimates for α are based on the assumption of average aggregate sizes of 0.01, 0.01, and 0.005 cm for Windsor, Olivier, and Cecil soils, respectively. In addition, D^a for Cr diffusion was assumed to be 10⁻⁹ cm² s⁻¹ for all three soils. Barber (1984) compiled diffusion coefficients for a number of ions in soils with values for phosphate (H₂PO₄⁻) ranging from 10⁻⁸ to 10⁻¹ cm² s⁻¹ (for water $D^a = 10^{-6}$ cm² s⁻¹). These values of D^a and μ were also used to estimate the hydrodynamic dispersion coefficient (D^m) in the mobile-water region using (Parker and Valocchi 1986, eq 46)

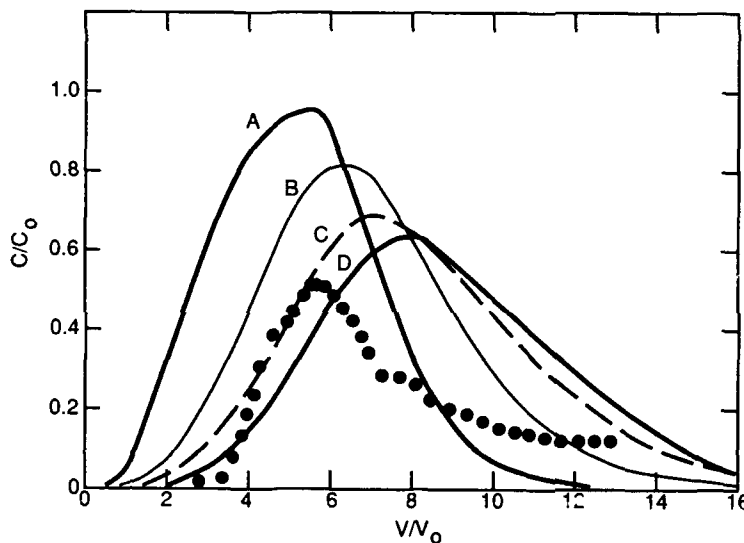
$$D^m = (1/\mu) [D - (1-\mu) a^2 v^2 / 15 D^a] \quad (9-8)$$

where v is the pore water velocity (n/Θ^m). Values for the dispersion coefficient D used in the above equation were averages of those obtained from BTCs of tritium and chloride-36 tracers. We should mention that attempts to use ³H₂O and ³⁶Cl BTCs for parameter estimation of α and D^m were not successful. Values obtained using the optimization method of van Genuchten (1981) were inconsistent and ill-defined due to large parameter standard errors and were often physically unrealistic (e.g., $R \gg 1$). Perhaps these results are due to local equilibrium conditions between the mobile and immobile regions for the two tracers (Rubin 1983, Parker and Valocchi 1986). Tailing of BTCs was not observed from the tracer results.

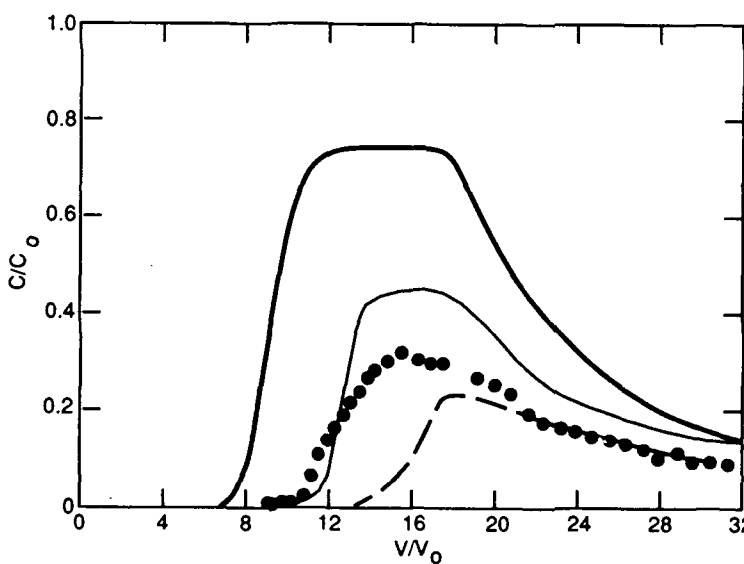
Values for the rate coefficients used in the SOMIM were those calculated from the batch kinetic results. Specifically, we used the k_1 , k_2 , and k_s values given in Tables 9-3 through 9-5 obtained from the three-parameter version of the second-order two-site model as described in Chapter 7. Predicted BTCs were obtained using different sets of batch rate coefficients due to their strong dependence on input concentrations (C_0 s). The closest predictions to experimental Cr measurements were obtained from batch rate coefficients at low C_0 values ($C_0 \leq 10$ mg L⁻¹). Moreover, the use of rate coefficients at higher C_0 s resulted in decreased tailing and reduced retardation of the BTCs.



a. Olivier soil. C/C_0 of curves A-D are 25, 10, 5, and 1 mg L^{-1} , respectively.



b. Windsor soil. C/C_0 of curves A-D are 25, 5, 2, and 1 mg L^{-1} , respectively.



c. Cecil soil. C/C_0 of curves A-C are 25, 10, and 5 mg L^{-1} , respectively.

Figure 9-6. Effluent concentration distributions for Cr predicted using the SOMIM with the batch rate coefficients indicated.

These observations are consistent with previous predictions using the SOTS model (Fig. 9-5). However, overall predictions of measured Cr using the SOMIM is considered less than adequate in comparison to SOTS model predictions. Reasons for the less-than-adequate predictions of BTCs for the three soils using the SOMIM are not fully understood. It is conceivable that a set of applicable rate coefficients over the concentration range for Cr transport experiments cannot be obtained simply by use of the batch procedure described in this study. In addition, several parameters used in model calculations were estimated and not measured, e.g., Θ''' , α , and D''' . The fraction of active sites f''' was not estimated, rather it was assumed equal to the mobile water fraction (Θ'''/Θ) since no means of its direct measurement was available. It is likely that improved BTC predictions could be obtained by use of parameter optimization, but such attempts were not performed. Other possible factors responsible for these predictions may be due in part to lack of nonequilibrium conditions between the mobile and immobile fractions for the SOMIM (Valocchi 1985, Parker and Valocchi 1986).

Based on the above analysis, we demonstrated the capability of a proposed second-order two-site (SOTS) model to describe Cr(VI) kinetic (batch) behavior in three soils. Reactions that were postulated to account for the observed kinetic behavior include formation of surface complexes between Cr(VI) and soil, reductive sorption or precipitation of Cr(VI), and internal diffusion. Moreover, the SOTS model was partly successful in predicting Cr miscible displacement results. The necessary model parameters, such as total amount of sites, fraction of sites, and rate coefficients, were not obtained by curve fitting, but were determined independently. A unique set of batch rate coefficients capable of predicting the BTCs were not obtained due to their strong dependence on input concentrations. When the proposed second-order approach was extended to the mobile-immobile (two-region) concept (SOMIM), little improvement in BTC predictions was achieved. The failure of the mobile-immobile model was attributed to the estimates for the model parameters and/or lack of nonequilibrium conditions in these soils. Additional validation of the SOMIM is needed.

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APPENDIX A: MRM

Computer Program Listing

```

1      C
2      C*****
3      C
4      C          P C   V E R S I O N   O F
5      C
6      C          ***** M. R. M. *****
7      C
8      C          M U L T I R E A C T I O N   M O D E L
9      C
10     C*****
11     C
12     C          C O M P U T E R   P R O G R A M
13     C
14     C          F O R
15     C
16     C          M U L T I   -   R E A C T I O N S
17     C
18     C          K I N E T I C   A N D   E Q U I L I B R I U M   R E T E N T I O N   O F
19     C
20     C          H E A V Y   M E T A L S   I N   S O I L S
21     C
22     C          U N D E R   B A T C H   R E A C T I O N   C O N D I T I O N S
23     C
24     C*****
25     C          P R O G R A M   W R I T T E N   A N D   D O C U M E N T E D
26     C
27     C          b y
28     C          H. M. SELLM
29     C
30     C          A p r i l   1 9 9 0
31     C*****
32     C --- DOUBLE PRECISION -----
33     C
34     C          IMPLICIT REAL*8(A-H,O-Z)
35     C          CHARACTER*64 FNAME1,FNAMEO
36     C          CHARACTER*64 USER,SOIL,SOLUTE,DATE
37     C          DIMENSION USER(15),SOIL(15),SOLUTE(15),DATE(15)
38     C          REAL*8 NEQ,KD,K1,K2,K3,K4,KS,K5,K6
39     C
40     C          WRITE(*,100)
41     C --- READ INPUT PARAMETERS -----
42     C
43     C          WRITE(*,*) ' PLEASE ENTER USER NAME (OPTIONAL):'
44     C          READ(*,200) USER
45     C          WRITE(*,*) ' PLEASE ENTER NAME OF SOIL (OPTIONAL):'
46     C          READ(*,200) SOIL
47     C          WRITE(*,*) ' PLEASE ENTER NAME OF SOLUTE (OPTIONAL):'
48     C          READ(*,200) SOLUTE
49     C          WRITE(*,*) ' ENTER DATE OR OTHER IDENTIFICATION (OPTIONAL):'
50     C          READ(*,200) DATE
51     C          WRITE(*,*) ' '
52     C          WRITE(*,*)
53     C          $' ----- INPUT PARAMETERS SECTION -----'
54     C          WRITE(*,*) ' '
55     C          WRITE(*,*) ' INPUT PARAMETERS CAN BE PROVIDED IN TWO WAYS;'
56     C          WRITE(*,*) ' ENTER 1 if you wish to enter the input data using'
57     C          WRITE(*,*) ' the keyboard (i.e. interactively)'
58     C          WRITE(*,*) ' '
59     C          WRITE(*,*) ' OR'
60     C          WRITE(*,*) ' '
61     C          WRITE(*,*) ' ENTER 2 if an input data file is to be provided'
62     C          WRITE(*,*)
63     C          $' PLEASE ENTER EITHER 1 OR 2'
64     C          READ(*,400) IFLAG

```

```

64      IF(IFLAG.NE.1) THEN
65      WRITE(*, '(A)') '      PLEASE ENTER NAME OF INPUT FILE?'
66      WRITE(*,*) '(for example A:XX.DAT or C:UU.DAT for hard disk)'
67      READ(*, '(A)') FNAMEI
68      OPEN(5, FILE=FNAMEI)
69      READ(5, 350) TH, ROU, CS, KD, NEQ, K1, K2, W, K3, K4, U, KS, K5, K6
70      READ(5, 450) IT
71      READ(5, 350) TTOTAL, TPRINT, DT
72      ELSE
73
74      C      WRITE(*,*)
75      $'PLEASE ENTER THE FOLLOWING INPUT PARAMETERS : '
76      WRITE(*,*) ' '
77      WRITE(*,*)
78      $' (1) MOISTURE CONTENT, CM3/CM3          (TH)  ='
79      WRITE(*,*)
80      $'(Values usually less than 0.65 cm3/cm3) or (the soil solution '
81      WRITE(*,*)
82      $'ratio for batch experiments). Please enter your value NOW'
83      READ(*, 300) TH
84      WRITE(*,*)
85      $' (2) BULK DENSITY, G/CM3              (ROU)  ='
86      WRITE(*,*)
87      $'(Range of values 1.1 - 1.7 g/cm3) to use the soil:solution'
88      WRITE(*,*)
89      $'ratio for batch experiments. Please enter your value NOW'
90      READ(*, 300) ROU
91      WRITE(*,*)
92      $' (3) APPLIED CONCENTRATION, MG/L        (CS)  ='
93      READ(*, 300) CS
94      WRITE(*,*)
95      $' (4) DISTRIBUTION COFFICIENT, CM3/G      (KD)  ='
96      WRITE(*,*)
97      $'(Range of values 0 - 300 cm3/g) Enter your value NOW'
98      READ(*, 300) KD
99      WRITE(*,*)
100     $' (5) NONLINEAR FREUNDLICH PARAMETER, N (NEQ)  ='
101     WRITE(*,*) '(Range of values 0.3 - 0.9). Enter your value NOW'
102     READ(*, 300) NEQ
103     WRITE(*,*)
104     $' (6) FORWARD RATE REACTION, K1, HR-1   (K1)  ='
105     WRITE(*,*) '(Range of values 0.01 - 2 hr-1). Enter your value NOW'
106     READ(*, 300) K1
107     WRITE(*,*)
108     $' (7) BACKWARD RATE REACTION, K2, HR-1   (K2)  ='
109     WRITE(*,*) '(Range of values 0.01 - 5 hr-1). Enter your value NOW'
110     READ(*, 300) K2
111     WRITE(*,*)
112     $' (8) NONLINEAR KINETIC PARAMETER, W        (W)  ='
113     WRITE(*,*) '(Range of values 0.3 - 0.9). Enter your value NOW'
114     READ(*, 300) W
115     WRITE(*,*)
116     $' (9) FORWARD RATE REACTION, K3, HR-1   (K3)  ='
117     WRITE(*,*) '(Ranges from 0.0001 - 0.1 hr-1). Enter your value NOW'
118     READ(*, 300) K3
119     WRITE(*,*)
120     $' (10) BACKWARD RATE REACTION, K4, HR-1   (K4)  ='
121     WRITE(*,*) '(Ranges from 0.01 - 0.1 hr-1). Enter your value NOW'
122     READ(*, 300) K4
123     WRITE(*,*)
124     $' (11) NONLINEAR KINETIC PARAMETER, U        (U)  ='
125     WRITE(*,*) '(Range of values 0.3 - 0.9). Enter your value NOW'
126     READ(*, 300) U
127     WRITE(*,*)
128     $' (12) IRREVERSIBLE REACTION RATE, KS, HR-1 (KS)  ='
129     WRITE(*,*) '(Range is 0.0001 - 0.01 hr-1). Enter your value NOW'
130     READ(*, 300) KS
131     WRITE(*,*)
132     $' (13) FORWARD RATE REACTION, K5, HR-1   (K5)  ='
133     WRITE(*,*) '(Range is 0.0001 - 0.05 hr-1). Enter your value NOW'

```



```

134      READ(*,300) K5
135      WRITE(*,*)
136      $' (14) BACKWARD RATE REACTION, K6, HR-1 (K6) ='
137      WRITE(*,*) '(Range is 0.001 - 0.1 hr-1). Enter your value NOW'
138      READ(*,300) K6
139      WRITE(*,*)
140      $' (15) NUMBER OF ITERATIONS (IT) AN INTEGER (FROM 0 TO 9)'
141      READ(*,400) IT
142      WRITE(*,*)
143      $' (16) TOTAL SIMULATION TIME, HOURS (TTOTAL) ='
144      READ(*,300) TTOTAL
145      WRITE(*,*)
146      $' (17) PRINTOUT TIME DESIRED, HOURS (TPRINT) ='
147      READ(*,300) TPRINT
148      WRITE(*,*)
149      $' (18) INCREMENTAL TIME STEP, HOURS (DT) ='
150      WRITE(*,*)
151      $' A default value of Dt=0.02 is given '
152      READ(*,300) DDT
153      ENDIF
154      C
155      PIN=0.02
156      IF (DDT.NE.0.0) THEN
157      DT=DDT
158      ELSE
159      DT=PIN
160      ENDIF
161      C
162      WRITE(*,'(A)') ' PLEASE ENTER NAME OF OUTPUT FILE (FOR EXAMPLE
163      * B:ZZ.DAT)'
164      READ(*,'(A)') FNAMEO
165      OPEN(6,FILE=FNAMEO,STATUS='UNKNOWN')
166      C --- WRITE TITLE HEADING -----
167      WRITE(6,100)
168
169      C --- WRITE INPUT PARAMETERS -----
170      C
171      WRITE(6,200) USER
172      WRITE(6,200) SOIL
173      WRITE(6,200) SOLUTE
174      WRITE(6,200) DATE
175      WRITE(6,500) TH,ROU,CS,KD,NEQ,K1,K2,W,K3,K4,U,KS
176      WRITE(6,600) K5,K6,IT,TTOTAL,TPRINT,DT
177
178      C
179      WRITE(*,*) '----- Execution Begins -----'
180      WRITE(*,*) ' '
181      C --- INITIAL CONDITIONS (TIME = 0) -----
182      C
183      TIME=0.0D0
184      TI=DT
185      C=CS
186      CX=0.0D0
187      SINPUT=TH*CS
188      SE=0.0D0
189      S1=0.0D0
190      S2=0.0D0
191      S3=0.0D0
192      SEX=SE
193      S1X=S1
194      S2X=S2
195      S3X=S3
196      SIR=0.0D0
197
198      C --- CALCULATION OF OUTPUT TIME STEPS AND TOTAL OUTPUT -----
199      C
200      II=TPRINT/TI+0.5D0
201      JJ=TTOTAL/TI+0.5D0
202      KK=JJ/II+0.5D0
203      C --- WRITE SIMULATION OUTPUT DATA COLUMN HEADINGS -----

```

```

204 C
205 WRITE(6,700)
206 WRITE(*,700)
207 C
208 C --- BEGIN SIMULATION -----
209 C
210 C CALCULATION OF S-EQUILIBRIUM AT TIME ZERO -----
211 C
212 COE=C+(ROU/TH)*SE
213 CEX=C
214 C
215 C --- ITERATION FOR S-EQUILIBRIUM CALCULATIONS -----
216 C
217 IF(KD.EQ.0.0D0) GO TO 20
218 IF(COE.LT.10.0E-20) GO TO 20
219 5 CONTINUE
220 DO 10 IE=1,5
221 C=CEX
222 10 CEX=COE/(1+KD*(ROU/TH)*C**(NEQ-1.0))
223 IF(DABS((CEX-C)).LT.1.0D-06) GO TO 15
224 GO TO 5
225 15 C=CEX
226 SE=KD*C**NEQ
227 20 CONTINUE
228 C
229 C ----- CALCULATIONS AT TIMES GREATER THAN ZERO -----
230 IT=IT+1
231 DO 70 K=1,KK
232 DO 60 J=1,II
233 DO 30 I=1,IT
234 C
235 C --- EXPLICIT-IMPLICIT FINITE DIFFERENCE CALCULATIONS -----
236 C
237 X1=TI*(K1*((C+CX)/2)**W)-K2*(ROU/TH)*((S1+S1X)/2)
238 X2=TI*(K3*((C+CX)/2)**U)-K4*(ROU/TH)*((S2+S2X)/2)
239 X3=TI*KS*((C+CX)/2)
240 CX=C-(X1+X2+X3)
241 S1X=S1+X1*(TH/ROU)
242 S2X=S2+X2*(TH/ROU)+TI*(K6*((S3+S3X)/2)-K5*((S2+S2X)/2))
243 S3X=S3+TI*(K5*((S2+S2X)/2)-K6*((S3+S3X)/2))
244 30 CONTINUE
245 C=CX
246 S1=S1X
247 S2=S2X
248 S3=S3X
249 SIR=SIR+TI*KS*(TH/ROU)*C
250 C
251 C
252 C ----- ITERATION FOR SE CALCULATIONS -----
253 COE=C+(ROU/TH)*SE
254 IF(COE.LT.10.0E-20) GO TO 50
255 CEX=C
256 35 CONTINUE
257 DO 40 IE=1,5
258 C=CEX
259 40 CEX=COE/(1+KD*(ROU/TH)*C**(NEQ-1.0D0))
260 IF(DABS((CEX-C)).LT.1.0D-06) GO TO 45
261 GO TO 35
262 45 C=CEX
263 SE=KD*C**NEQ
264 CX=C
265 50 CONTINUE
266 C
267 C
268 60 CONTINUE
269 C
270 C --- MASS BALANCE CALCULATIONS -----
271 C
272 BAL=100*(C*TH+ROU*(SE+S1+S2+S3+SIR))/SINPUT
273 TOTALS=SE+S1+S2+S3+SIR

```

```

274 C
275 C --- WRITE OUTPUT DATA AT DESIRED SIMULATION TIMES -----
276 C
277 TIME=K*TPRINT
278 WRITE(6,800) TIME,C,SE,S1,S2,S3,SIR,TOTALS,BAL
279 WRITE(*,800) TIME,C,SE,S1,S2,S3,SIR,TOTALS,BAL
280 70 CONTINUE
281 C
282 C --- FORMAT STATEMENTS ---
283 C
284 C
285 100 FORMAT(/,7X,
286 &'*****',
287 $//,7X,
288 &' WELCOME TO ',
289 $//,7X,
290 &' P C V E R S I O N O F ',
291 $//,7X,
292 &' M. R. M. ',
293 $//,7X,
294 &' SIMULATION MODEL FOR KINETIC ',
295 $//,7X,
296 &' RETENTION OF HEAVY METALS IN SOILS ',
297 $//,7X,
298 &' UNDER NO - FLOW CONDITIONS ',
299 $//,7X,
300 $//,7X,
301 &'*****',
302 $/,7X,
303 &' PROGRAM WRITTEN AND DOCUMENTED ',
304 $/,7X,
305 &' by ',
306 $/,7X,
307 &' H. M. SELIM ',
308 $/,7X,
309 &' April 1990 ',
310 $/,7X,
311 &'*****',
312 &/)
313 200 FORMAT(A64)
314 300 FORMAT(F12.0)
315 350 FORMAT(50X,E20.6)
316 400 FORMAT(I1)
317 450 FORMAT(50X,I3)
318 500 FORMAT(/,
319 $2X,'INPUT PARAMETERS :',//
320 $5X,'1. MOISTURE CONTENT, CM3/CM3 (TH) =',F10.5,/
321 $5X,'2. BULK DENSITY, G/CM3 (ROU) =',F10.5,/
322 $5X,'3. APPLIED CONCENTRATION, MG/L (CS) =',F10.5,/
323 $5X,'4. DISTRIBUTION COEFFICIENT, KD,CM3/G (KD) =',F10.5,/
324 $5X,'5. NONLINEAR FREUNDLICH PARAMETER, N (NEQ) =',F10.5,/
325 $5X,'6. FORWARD RATE REACTION, K1,HR-1 (K1) =',F10.5,/
326 $5X,'7. BACKWARD RATE REACTION, K2,HR-1 (K2) =',F10.5,/
327 $5X,'8. NONLINEAR KINETIC PARAMETER, W, (W) =',F10.5,/
328 $5X,'9. FORWARD RATE REACTION, K3,HR-1 (K3) =',F10.5,/
329 $4X,'10. BACKWARD RATE REACTION, K4,HR-1 (K4) =',F10.5,/
330 $4X,'11. NONLINEAR KINETIC PARAMETER, U, (U) =',F10.5,/
331 $4X,'12. IRREVERSIBLE REACTION RATE,KS,HR-1 (KS) =',F10.5)
332 600 FORMAT(
333 $4X,'13. FORWARD RATE REACTION, K5,HR-1 (K5) =',F10.5,/
334 $4X,'14. BACKWARD RATE REACTION, K6,HR-1 (K6) =',F10.5,/
335 $4X,'15. NUMBER OF ITERATIONS, M (IT) =',I10,/
336 $4X,'16. TOTAL SIMULATION TIME,HOURS (TTOTAL) =',F10.5,/
337 $4X,'17. PRINTOUT TIME DESIRED,HOURS (TPRINT) =',F10.5,/
338 $4X,'18. INCREMENTAL TIME STEP,HOURS (DT) =',F10.5,////)
339 700 FORMAT(////,72(1H*)//1H,27X,'SIMULATION RESULTS'//,
340 172(1H*)//,1X,
341 *'TIME SOLUTION EQUIL KINETIC KINETIC KINETIC IRREV. TOTAL
342 * MASS',8X,'CONC.',3X,
343 *'PHASE PHASE 1 PHASE 2 PHASE 3 SINK SORBED BALANCE'//,

```

```

344      *'T      C      SE      S1      S2      S3      SIR      S
345      *      '///,
346      4X, '--MG/L--', 4X,
347      1'-----MG/KG-----')
348      800  FORMAT(1X,F6.1,1X,F8.4,1X,F7.4,1X,F7.3,
349      *1X,3(F8.3,1X),F7.3,1X,F7.2)
350      WRITE(*,*)
351      WRITE(*,*) '----- Requested Simulations Completed -----'
352      WRITE(*,*)
353      WRITE(*,*) '----- MRM TERMINATED SUCCESSFULLY -----'
354      WRITE(*,*)
355      WRITE(*,*) '----- THANK YOU FOR USING MRM -----'
356      END

```

Sample of MRM Input Data

1.	MOISTURE CONTENT, CM3/CM3	(TH) =	0.500E00
2.	BULK DENSITY, G/CM3	(ROU) =	1.250E00
3.	APPLIED CONCENTRATION, MG/L	(CS) =	10.000E00
4.	DISTRIBUTION COEFFICIENT, KD, CM3/G	(KD) =	1.000E00
5.	NONLINEAR FREUNDLICH PARAMETER, N	(NEQ) =	0.500E00
6.	FORWARD RATE REACTION, K1, HR-1	(K1) =	0.010E00
7.	BACKWARD RATE REACTION, K2, HR-1	(K2) =	0.100E00
8.	NONLINEAR KINETIC PARAMETER, W	(W) =	0.750E00
9.	FORWARD RATE REACTION, K3, HR-1	(K3) =	0.100E00
10.	BACKWARD RATE REACTION, K4, HR-1	(K4) =	0.100E00
11.	NONLINEAR KINETIC PARAMETER, U	(U) =	0.900E00
12.	IRREVERSIBLE REACTION RATE, KS, HR-1	(KS) =	0.001E00
13.	FORWARD RATE REACTION, K5, HR-1	(K5) =	0.010E00
14.	BACKWARD RATE REACTION, K6, HR-1	(K6) =	0.100E00
15.	NUMBER OF ITERATIONS, M	(IT) =	000
16.	TOTAL SIMULATION TIME, HOURS	(TTOTAL) =	50.000E00
17.	PRINTOUT TIME DESIRED, HOURS	(TPRINT) =	1.000E00
18.	TIME STEP, HOURS	(DT) =	0.100E00

MRM Computer Program Output Listing

WELCOME TO

P C VERSION OF

M. R. M.

SIMULATION MODEL FOR KINETIC

RETENTION OF HEAVY METALS IN SOILS

UNDER NO - FLOW CONDITIONS

PROGRAM WRITTEN AND DOCUMENTED

by

H. M. SELIM

February 1990

INPUT PARAMETERS :

1.	MOISTURE CONTENT, CM3/CM3	(TH)	=	.50000
2.	BULK DENSITY, G/CM3	(ROU)	=	1.25000
3.	APPLIED CONCENTRATION, MG/L	(CS)	=	10.00000
4.	DISTRIBUTION COEFFICIENT, KD, CM3/G (KD)		=	1.00000
5.	NONLINEAR FREUNDLICH PARAMETER, N (NEQ)		=	.50000
6.	FORWARD RATE REACTION, K1, HR-1	(K1)	=	.01000
7.	BACKWARD RATE REACTION, K2, HR-1	(K2)	=	.10000
8.	NONLINEAR KINETIC PARAMETER, W,	(W)	=	.75000
9.	FORWARD RATE REACTION, K3, HR-1	(K3)	=	.10000
10.	BACKWARD RATE REACTION, K4, HR-1	(K4)	=	.10000
11.	NONLINEAR KINETIC PARAMETER, U,	(U)	=	.90000
12.	IRREVERSIBLE REACTION RATE, KS, HR-1	(KS)	=	.00100
13.	FORWARD RATE REACTION, K5, HR-1	(K5)	=	.01000
14.	BACKWARD RATE REACTION, K6, HR-1	(K6)	=	.10000
15.	NUMBER OF ITERATIONS, M	(IT)	=	. 0
16.	TOTAL SIMULATION TIME, HOURS	(TTOTAL)	=	50.00000
17.	PRINTOUT TIME DESIRED, HOURS	(TPRINT)	=	1.00000
18.	INCREMENTAL TIME STEP, HOURS	(DT)	=	.02000

SIMULATION RESULTS

TIME	SOLUTION	EQUIL	KINETIC	KINETIC	KINETIC	IRREV.	TOTAL	MASS
	CONC.	PHASE	PHASE 1	PHASE 2	PHASE 3	SINK	SORBED	BALANCE
T	C	SE	S1	S2	S3	SIR	S	
	--MG/L--			-----MG/KG-----				
1.0	4.3731	2.0912	.012	.145	.001	.002	2.251	100.00
2.0	4.1572	2.0389	.022	.270	.003	.003	2.337	100.00
3.0	3.9730	1.9932	.031	.376	.006	.005	2.411	100.00
4.0	3.8154	1.9533	.038	.467	.009	.007	2.474	100.00
5.0	3.6803	1.9184	.045	.543	.013	.008	2.528	100.00
6.0	3.5642	1.8879	.051	.609	.017	.010	2.574	100.00
7.0	3.4643	1.8613	.056	.665	.022	.011	2.614	100.00
8.0	3.3781	1.8380	.060	.712	.026	.012	2.649	100.00
9.0	3.3036	1.8176	.064	.753	.031	.014	2.679	100.00
10.0	3.2390	1.7997	.067	.788	.035	.015	2.704	100.00
11.0	3.1829	1.7841	.070	.818	.039	.016	2.727	100.00
12.0	3.1341	1.7703	.072	.843	.044	.018	2.746	100.00
13.0	3.0916	1.7583	.074	.865	.048	.019	2.763	100.00
14.0	3.0544	1.7477	.076	.883	.051	.020	2.778	100.00
15.0	3.0219	1.7384	.077	.899	.055	.021	2.791	100.00
16.0	2.9933	1.7301	.079	.913	.058	.022	2.803	100.00
17.0	2.9682	1.7228	.080	.925	.062	.024	2.813	100.00
18.0	2.9460	1.7164	.081	.935	.065	.025	2.822	100.00
19.0	2.9265	1.7107	.082	.944	.067	.026	2.830	100.00
20.0	2.9091	1.7056	.082	.951	.070	.027	2.836	100.00
21.0	2.8938	1.7011	.083	.958	.072	.028	2.843	100.00
22.0	2.8801	1.6971	.084	.963	.075	.030	2.848	100.00
23.0	2.8679	1.6935	.084	.968	.077	.031	2.853	100.00
24.0	2.8570	1.6903	.084	.972	.079	.032	2.857	100.00
25.0	2.8472	1.6874	.085	.976	.080	.033	2.861	100.00
26.0	2.8384	1.6847	.085	.979	.082	.034	2.865	100.00
27.0	2.8305	1.6824	.085	.981	.084	.035	2.868	100.00
28.0	2.8233	1.6803	.085	.984	.085	.036	2.871	100.00
29.0	2.8168	1.6783	.086	.986	.086	.037	2.873	100.00
30.0	2.8109	1.6766	.086	.987	.087	.039	2.876	100.00
31.0	2.8056	1.6750	.086	.989	.089	.040	2.878	100.00
32.0	2.8007	1.6735	.086	.990	.090	.041	2.880	100.00
33.0	2.7962	1.6722	.086	.991	.090	.042	2.882	100.00
34.0	2.7921	1.6710	.086	.992	.091	.043	2.883	100.00
35.0	2.7883	1.6698	.086	.993	.092	.044	2.885	100.00
36.0	2.7848	1.6688	.086	.993	.093	.045	2.886	100.00
37.0	2.7815	1.6678	.086	.994	.093	.046	2.887	100.00
38.0	2.7785	1.6669	.086	.994	.094	.048	2.889	100.00
39.0	2.7757	1.6660	.086	.995	.094	.049	2.890	100.00
40.0	2.7730	1.6652	.086	.995	.095	.050	2.891	100.00
41.0	2.7705	1.6645	.086	.995	.095	.051	2.892	100.00
42.0	2.7682	1.6638	.086	.995	.096	.052	2.893	100.00
43.0	2.7660	1.6631	.086	.995	.096	.053	2.894	100.00
44.0	2.7639	1.6625	.086	.995	.096	.054	2.894	100.00
45.0	2.7619	1.6619	.086	.995	.097	.055	2.895	100.00
46.0	2.7600	1.6613	.086	.995	.097	.056	2.896	100.00
47.0	2.7582	1.6608	.086	.995	.097	.057	2.897	100.00
48.0	2.7565	1.6603	.086	.995	.097	.059	2.897	100.00
49.0	2.7548	1.6598	.086	.995	.098	.060	2.898	100.00
50.0	2.7532	1.6593	.086	.995	.098	.061	2.899	100.00

APPENDIX B: MRTM **Computer Program Listing**

```

1      C
2      C*****
3      C
4      C          ***** M. R. T. M. *****
5      C
6      C*****
7      C
8      C          COMPUTER PROGRAM
9      C
10     C          FOR THE SIMULTANEOUS TRANSPORT AND RETENTION
11     C                OF HEAVY METALS
12     C                IN THE SOIL PROFILE
13     C                USING
14     C          THE SOLUTE CONVECTION - DISPERSION EQUATION
15     C                AND
16     C                MULTIREACTION MECHANISMS
17     C                OF
18     C          NONLINEAR EQUILIBRIUM AND KINETIC REACTIONS
19     C
20     C
21     C*****
22     C          PROGRAM WRITTEN AND DOCUMENTED
23     C                H. M. SELIM
24     C                by
25     C                1990
26     C*****
27     C
28     C          IMPLICIT REAL*8(A-H,O-Z)
29     C          CHARACTER*64 FNAMEI,FNAMEO
30     C          COMMON/L1/ C(101),DC(101),DU(101),DL(101),E(101),S1(101),S2(101)
31     C          COMMON/L2/ SIR(101),CX(101),S1X(101),S2X(101)
32     C          COMMON/L3/ X(101),S3(101),S3X(101)
33     C          COMMON/L4/ TH,ROU,COL,WFLX,CI,CS,D,K1,K2,W,K3,K4,U,KS,K5,K6,KD
34     C          COMMON/L5/ NEQ,IT,N,NM1,NP1
35     C          COMMON/L6/ TPULSE,TTOTAL,TPRINT,DT,DX,GAMMA,BETA
36     C          CHARACTER*64 USER,SOIL,SOLUTE,DATE
37     C          REAL*8 K1,K2,K3,K4,K5,K6,KS,KD,NEQ
38     C
39     C
40     C          WRITE(*,100)
41     C --- READ INPUT PARAMETERS -----
42     C
43     C          WRITE(*,*) ' PLEASE ENTER USER NAME (OPTIONAL): '
44     C          READ(*,800) USER
45     C          WRITE(*,*) ' PLEASE ENTER NAME OF SOIL (OPTIONAL): '
46     C          READ(*,800) SOIL
47     C          WRITE(*,*) ' PLEASE ENTER NAME OF SOLUTE (OPTIONAL): '
48     C          READ(*,800) SOLUTE
49     C          WRITE(*,*) ' ENTER DATE OR OTHER IDENTIFICATION (OPTIONAL): '
50     C          READ(*,800) DATE
51     C          WRITE(*,*) ' '
52     C          WRITE(*,*) ' '
53     C          $' ----- INPUT PARAMETERS SECTION -----'
54     C          WRITE(*,*) ' '
55     C          WRITE(*,*) ' INPUT PARAMETERS CAN BE PROVIDED IN TWO WAYS; '
56     C          WRITE(*,*) ' ENTER 1 if you wish to enter the input data using '
57     C          WRITE(*,*) ' the keyboard (i.e. interactively) '
58     C          WRITE(*,*) ' '
59     C          WRITE(*,*) ' OR '
60     C          WRITE(*,*) ' '
61     C          WRITE(*,*) ' ENTER 2 if an input data file is to be provided '
62     C          WRITE(*,*) ' '
63     C          $' PLEASE ENTER EITHER 1 OR 2 '
64     C          READ(*,950) IFLAG
65     C          IF(IFLAG.NE.1) THEN
66     C          WRITE(*,'(A)') ' PLEASE ENTER NAME OF INPUT FILE? '
67     C          WRITE(*,*) '(for example A:XX.DAT or C:UU.DAT for hard disk) '
68     C          READ(*,'(A)') FNAMEI
69     C          OPEN(5,FILE=FNAMEI)
70     C

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```

71      C
72      READ(5,700) TH,ROU,COL,WFLX
73      READ(5,700) CI,CS,D
74      READ(5,700) KD,NEQ
75      READ(5,700) K1,K2,W
76      READ(5,700) K3,K4,U
77      READ(5,700) KS
78      READ(5,700) K5,K6
79      READ(5,750) IT
80      READ(5,700) TPULSE,TTOTAL,TPRINT,DT,DX
81      ELSE
82      C
83      WRITE(*,*)
84      $'PLEASE ENTER THE FOLLOWING INPUT PARAMETERS : '
85      WRITE(*,*) ' '
86      WRITE(*,*)
87      $' (1) MOISTURE CONTENT, CM3/CM3 (TH) ='
88      WRITE(*,*)
89      $'(Values usually less than 0.65 cm3/cm3). Enter your value NOW'
90      READ(*,900) TH
91      WRITE(*,*)
92      $' (2) BULK DENSITY, G/CM3 (ROU) ='
93      WRITE(*,*)
94      $'(Range of values 1.1 - 1.7 g/cm3). Enter your value NOW'
95      READ(*,900) ROU
96      WRITE(*,*)
97      $' (3) PROFILE OR SOIL COLUMN LENGTH, CM (COL) ='
98      READ(*,900) COL
99      WRITE(*,*)
100     $' (4) WATER FLUX, CM/HOUR (WFLX) ='
101     WRITE(*,*)
102     $'(Range of values 0.01 - 5 cm/hr). Enter your value NOW'
103     READ(*,900) WFLX
104     WRITE(*,*)
105     $' (5) INITIAL CONCENTRATION, MG/L (CI) ='
106     READ(*,900) CI
107     WRITE(*,*)
108     $' (6) APPLIED CONCENTRATION, MG/L (CS) ='
109     READ(*,900) CS
110     WRITE(*,*)
111     $' (7) DISPERSION COEFFICIENT,D, CM2/HOUR (D) ='
112     WRITE(*,*)
113     $'(Range of values 0.1 - 1.5 cm2/hour). Enter your value NOW'
114     READ(*,900) D
115     WRITE(*,*)
116     $' (8) DISTRIBUTION COEFFICIENT, KD (KD) ='
117     WRITE(*,*)
118     $'(Range of values 0 - 300 cm3/g) Enter your value NOW'
119     READ(*,900) KD
120     WRITE(*,*)
121     $' (9) NONLINEAR FREUNDLICH PARAMETER, N (NEQ) ='
122     WRITE(*,*) $'(Range of values 0.3 - 0.9). Enter your value NOW'
123     READ(*,900) NEQ
124     WRITE(*,*)
125     $' (10) FORWARD RATE REACTION, K1, HR-1 (K1) ='
126     WRITE(*,*) $'(Range of values 0.01 - 2 hr-1). Enter your value NOW'
127     READ(*,900) K1
128     WRITE(*,*)
129     $' (11) BACKWARD RATE REACTION, K2, HR-1 (K2) ='
130     WRITE(*,*) $'(Range of values 0.01 - 5 hr-1). Enter your value NOW'
131     READ(*,900) K2
132     WRITE(*,*)
133     $' (12) NONLINEAR KINETIC PARAMETER, W, (W) ='
134     WRITE(*,*) $'(Range of values 0.3 - 0.9). Enter your value NOW'
135     READ(*,900) W
136     WRITE(*,*)
137     $' (13) FORWARD RATE REACTION, K3, HR-1 (K3) ='
138     WRITE(*,*) $'(Ranges from 0.0001 - 0.1 hr-1). Enter your value NOW'
139     READ(*,900) K3
140     WRITE(*,*)
141     $' (14) BACKWARD RATE REACTION, K4, HR-1 (K4) ='
142     READ(*,900) K4
143     WRITE(*,*) $'(Ranges from 0.01 - 0.1 hr-1). Enter your value NOW'
144     WRITE(*,*)
145     $' (15) NONLINEAR KINETIC PARAMETER, U, (U) ='
146     WRITE(*,*) $'(Range of values 0.3 - 0.9). Enter your value NOW'

```

```

147         READ(*,900) U
148         WRITE(*,*)
149         $' (16) IRREVERSIBLE REACTION RATE,KS,HR-1 (K5) ='
150         WRITE(*,*) '(Range is 0.0001 - 0.01 hr-1). Enter your value NOW'
151         READ(*,900) K5
152         WRITE(*,*)
153         $' (17) FORWARD RATE REACTION, K5,H R-1 (K5) ='
154         WRITE(*,*) '(Range is 0.0001 - 0.05 hr-1). Enter your value NOW'
155         READ(*,900) K5
156         WRITE(*,*)
157         $' (18) BACKWARD RATE REACTION, K6, HR-1 (K6) ='
158         WRITE(*,*) '(Range is 0.001 - 0.1 hr-1). Enter your value NOW'
159         READ(*,900) K6
160         WRITE(*,*)
161         $' (19) NUMBER OF ITERATIONS (IT) AN INTEGER (FROM 0 TO 9)'
162         READ(*,950) IT
163         WRITE(*,*)
164         $' (20) INPUT PULSE DURATION, HOURS (TPULSE) ='
165         READ(*,900) TPULSE
166         WRITE(*,*)
167         $' (21) TOTAL SIMULATION TIME, HOURS (TTOTAL) ='
168         READ(*,900) TTOTAL
169         WRITE(*,*)
170         $' (22) PRINTOUT TIME DESIRED, HOURS (TPRINT) ='
171         READ(*,900) TPRINT
172         WRITE(*,*)
173         $' (23) INCREMENTAL TIME STEP, HOURS (DT) ='
174         WRITE(*,*)
175         $' A default value of DT=0.02 is given '
176         READ(*,900) DDT
177         WRITE(*,*)
178         $' (24) INCREMENTAL DEPTH, CM (DX) ='
179         WRITE(*,*)
180         $' A default value of DX=1.00 is given '
181         READ(*,900) DDX
182         ENDIF
183
184         C
185         XIN=1.00
186         IF (DDX.NE.0.0) THEN
187             DX=DDX
188         ELSE
189             DX=XIN
190         ENDIF
191
192         C
193         PIN=0.02
194         IF (DDT.NE.0.0) THEN
195             DT=DDT
196         ELSE
197             DT=PIN
198         ENDIF
199         WRITE(*, '(A)') ' PLEASE ENTER NAME OF OUTPUT FILE (FOR EXAMPLE
200         * B:ZZ.DAT)'
201         READ(*, '(A)') FNAMEO
202         OPEN(6, FILE=FNAMEO, STATUS='UNKNOWN')
203         PV=WFLX/TH
204         RS=NEQ*ROU*KD/TH
205         CO=CS
206
207         C
208         TIME=0.0D0
209         EF=0.0D0
210
211         5 CONTINUE
212         GAMMA=DT/(2.0D0*DX*DX)
213         BETA=DT/DX
214         IF ((BETA*PV).GT.0.5D0) GO TO 7
215         IF ((GAMMA*D/(BETA*PV)).LT.0.5D0) GO TO 6
216         GO TO 8
217
218         6 DX=DX/2
219         GO TO 5
220
221         7 DT=DT/2
222         GO TO 5
223
224         8 CONTINUE
225         N=COL/DX
226         NM1=N-1
227         NM2=N-2
228         NP1=N+1
229         GAMMA=DT/(2*DX*DX)

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```

223      BETA=DT/DX
224      C
225      IF(N.LT.500) GO TO 9
226      WRITE(*,*) ' W A R N I N G '
227      WRITE(*,*)
228      &'Dimension of variables exceeds 500. Did you increase array
        sizes'
229      WRITE(*,*)
230      &' If not, the program will terminate abruptly (see text).'
231      9  CONTINUE
232      C
233      C --- WRITE TITLE HEADING -----
234      WRITE(6,100)
235      WRITE(6,800) USER
236      WRITE(6,800) SOIL
237      WRITE(6,800) SOLUTE
238      WRITE(6,800) DATE
239      WRITE(6,300) TH,ROU,COL,WFLX,CI,CS,D,K1,K2,B,K3,K4,W,KS
240      WRITE(6,310) K5,K6,IT,KD,NEQ
241      &,TPULSE,TTOTAL,TPRINT
242      WRITE(6,400) DX,DT
243      C
244      DO 10 I=1,NP1
245      S1(I)=0.0D0
246      S2(I)=0.0D0
247      S3(I)=0.0D0
248      SIR(I)=0.0D0
249      S1X(I)=0.0D0
250      S2X(I)=0.0D0
251      S3X(I)=0.0D0
252      CX(I)=CI
253      10  C(I)=CI
254      WRITE(*,*) '----- INITIAL CONDITIONS COMPLETED -----'
255      C
256      WRITE(*,*) '----- Execution Begins -----'
257      WRITE(*,*) '----- Please Wait -----'
258      IT=IT+1
259      FF=2*DX
260      NKK=TPRINT/DT+0.5D0
261      KLM=TTOTAL/DT+0.5D0
262      KK=KLM/NKK+0.5D0
263      C
264      L=0
265      SINT=TPULSE*COL*WFLX
266      DO 50 JJ=1,KK
267      DO 20 LL=1,NKK
268      TT=LL*DT+(JJ-1)*TPRINT
269      IF (DABS(TT-TPULSE).LT.0.01D0) CS=0.0D0
270      L=L+1
271      CALL SMRTM
272      EF=C(N)+EF
273      20  CONTINUE
274      TIME=JJ*TPRINT
275      C
276      WRITE(6,500) TIME
277      VV0=WFLX*TIME/(COL*TH)
278      CC0=C(N)/C0
279      WRITE(6,525) VV0,CC0
280      WRITE(*,650) TIME,VV0,CC0
281      WRITE(*,*) '----- Execution Continues -----'
282      WRITE(*,*) '----- Please Wait -----'
283      WRITE(6,550)
284      DO 30 I=1,NP1
285      DEPTH=DX*(I-1)
286      SEQ=KD*C(I)**NEQ
287      TOTAL=SEQ+S1(I)+S2(I)+S3(I)+SIR(I)
288      30  WRITE(6,600) DEPTH,C(I),SEQ,S1(I),S2(I),S3(I),SIR(I),TOTAL
289      CALL INTEG(DX,C,NEQ,NP1)
290      TSWATR=TH*X(NP1)
291      C
292      DO 40 I=1,NP1
293      40  E(I)=C(I)**NEQ
294      CALL INTEG(DX,E,X,NP1)
295      TSEQ=ROU*KD*X(NP1)
296      SINP=TIME*CS*WFLX
297      IF (SINP.GT.SINT) SINP=SINT

```

```

298      IF(CS.EQ.0.D0) SINP=SINT
299      C
300      CALL INTEG(DX,S1,X,NP1)
301      TSKIN1=POU*X(NP1)
302      C
303      CALL INTEG(DX,S2,X,NP1)
304      TSKIN2=ROU*X(NP1)
305      C
306      CALL INTEG(DX,S3,X,NP1)
307      TSKIN3=ROU*X(NP1)
308      C
309      TEFFL=DT*WFLX*EF
310      C
311      CALL INTEG(DX,SIR,X,NP1)
312      TSIR=ROU*X(NP1)
313      BAL=(TEFFL+TSKIN1+TSKIN2+TSKIN3+TSIR+TSEQ+TSWATR)*100.0D0/SINP
314      WRITE(6,200) SINP,TSWATR,TSEQ,TSKIN1,TSKIN2,TSKIN3,TSIR,TEFFL,BAL
315      50  CONTINUE
316      C
317      100  FORMAT(//,7X,
318
319          &'*****
320          $//,7X,
321          &'
322          $//,7X,
323          &'*****',
324          &'      SIMULATION RESULTS USING MRTM MODEL FOR TRANSPORT
325          $//,7X,
326          &'
327          $//,7X,
328          &'      RETENTION OF HEAVY METALS IN THE SOIL
329          $//,7X,
330          &'
331          $//,7X,
332          &'      STEADY WATER FLOW CONDITIONS
333          $//,7X,
334          $//,7X,
335          &'*****
336          $//,7X,
337          &'      PROGRAM WRITTEN AND DOCUMENTED
338          $//,7X,
339          &'
340          $//,7X,
341          &'
342          $//,7X,
343          &'
344          $//,7X,
345          &'*****
346          200  FORMAT(//,2X,'S A L T   B A L A N C E :',//
347          &'7X,'TOTAL INPUT SOLUTE FROM PULSE      (MG)  =',F10.4,/
348          &'7X,'TOTAL SOLUTE SOIL SOLUTION PHASE (MG)  =',F10.4,/
349          &'7X,'TOTAL SORBED IN (EQUILIB) PHASE SE (MG)  =',F10.4,/
350          &'7X,'TOTAL SORBED IN (KINETIC) PHASE S1 (MG)  =',F10.4,/
351          &'7X,'TOTAL SORBED IN (KINETIC) PHASE S2 (MG)  =',F10.4,/
352          &'7X,'TOTAL SORBED IN (KINETIC) PHASE S3 (MG)  =',F10.4,/
353          &'7X,'TOTAL SORBED IN IRREVERSIBLE PHASE (MG) =',F10.4,/
354          &'7X,'TCTAL SOLUTE IN THE EFFLUENT      (MG)  =',F10.4,/
355          &'7X,'MASS BALANCE (CALC.OUTPUT/INPUT)    (*)  =',F10.4,/
356          300  FORMAT(//,
357          $2X,'INPUT PARAMETERS :',//

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```

358      $5X,'1.    MOISTURE CONTENT,CM3/CM3          (TH)    =' ,F10.5,/
359      $5X,'2.    BULK DENSITY,G/CM3              (ROU)    =' ,F10.5,/
360      $5X,'3.    COLUMN LENGTH,CM                (COL)    =' ,F10.5,/
361      $5X,'4.    WATER FLUX,CM/HOUR              (WFLX)   =' ,F10.5,/
362      $5X,'5.    INITIAL CONCENTRATION,MG/L        (CI)     =' ,F10.5,/
363      $5X,'6.    CONCEN.IN INPUT PULSE,MG/L        (CS)     =' ,F10.5,/
364      $5X,'7.    DISPERSION COEFFICIENT,CM2/HR      (D)      =' ,F10.5,/
365      $5X,'8.    FORWARD RATE REACTION, K1,HR-1    (K1)     =' ,F10.5,/
366      $5X,'9.    BACKWARD RATE REACTION, K2,HR-1    (K2)     =' ,F10.5,/
367      $4X,'10.   NONLINEAR KINETIC PARAMETER, W,    (W)      =' ,F10.5,/
368      $4X,'11.   FORWARD RATE REACTION, K3,HR-1    (K3)     =' ,F10.5,/
369      $4X,'12.   BACKWARD RATE REACTION, K4,HR-1    (K4)     =' ,F10.5,/
370      $4X,'13.   NONLINEAR KINETIC PARAMETER, U,    (U)      =' ,F10.5,/
371      $4X,'14.   IRREVERSIBLE REACTION RATE,KS,HR-1 (KS)     =' ,F10.5)
372
373      310  FORMAT(
374      $4X,'15.   FORWARD RATE REACTION, K5,HR-1    (K5)     =' ,F10.5,/
375      $4X,'16.   BACKWARD RATE REACTION, K6,HR-1    (K6)     =' ,F10.5,/
376      $4X,'17.   NUMBER OF ITERATIONS              (IT)     =' ,I10,/
377      $4X,'18.   DISTRIBUTION COEFFICIENT FOR EQUILIBRIUM',/
378      $4X,'      SORPTION, KD, CM3/G                (KD)     =' ,F10.5,/
379      $4X,'19.   NONLINEAR PARAMETER FOR EQUILIBRIUM',/
380      $4X,'      MECHANISM, NEQ                      (NEQ)     =' ,F10.5,/
381      $4X,'20.   INPUT PULSE DURATION,HR            (TPULSE)   =' ,F10.5,/
382      $4X,'21.   TOTAL SIMULATION TIME,HR           (TTOTAL)  =' ,F10.5,/
383      $4X,'22.   PRINTOUT TIME DESIRED,HR           (TPRINT)
384      =' ,F10.5,////)
385
386      400  FORMAT(2X,'THE INCREMENTS USED WERE :',//
387      $5X,'1. SIMULATION DEPTH INTERVAL,CM          (DX)     =' ,F10.5,/
388      $5X,'2. INCREMENTAL TIME STEP,HR              (DT)     =' ,F10.5,////)
389
390      500  FORMAT(/////////,
391      $2X'S I M U L A T I O N      T I M E (HOUR)    =' ,F8.2/)
392
393      525  FORMAT(
394      $2X'PORE VOLUMES (V/V0) =' ,F10.2,$X.'REL. CONCENTRATION (C/C0) =' ,
395      &F8.4)
396
397      550  FORMAT(///1H ,72(1H*)//1H ,20X,'CONCENTRATION DISTRIBUTION',
398      *//1H ,
399      172(1H*)//1H ,2X,
400      *'DEPTH      SOLUT      EQUIL      KINETIC      KINETIC      KINETIC      IRREV.
401      * TOTAL'/ ,9X,'CONC.' ,4X,
402      *'PHASE      PHASE 1    PHASE 2    PHASE 3    SINK      SORBED'//,
403      *' X          C          SE        S1         S2         S3          SIR
404      *
405      S'// ,1X
406      1, ' CM ' ,2X,'--MG/L--' ,2X,
407      1'-----MG/KG-----')
408
409      600  FORMAT(1X,F6.2,1X,F9.4,1X,F8.4,1X,F8.3,
410      *1X,3(F9.3,1X),F7.3)
411
412      650  FORMAT(////////,2X,'SIMULATIONS ARE NOW COMPLETE UP TO',///,5X,
413      $'S I M U L A T I O N      T I M E (HOUR)    =' ,F8.2,///2X,
414      $'PORE VOLUMES (V/V0) =' ,F10.2,$X,'REL. CONCENTRATION (C/C0) =' ,
415      &F8.4//)
416
417      700  FORMAT(50X,E10.6)
418      750  FORMAT(50X,I3)
419      800  FORMAT(A64)
420      900  FORMAT(F12.0)
421      950  FORMAT(I1)
422      WRITE(*,*)
423      WRITE(*,*) '----- Requested Simulations Completed -----'
424      WRITE(*,*)
425      WRITE(*,*) '----- MRTM TERMINATED SUCCESSFULLY -----'
426      WRITE(*,*)
427      WRITE(*,*) '----- THANK YOU FOR USING MRTM -----'
428      END
429
430      C
431      C
432      C *****
433      C SUBROUTINE TRIDM GIVES A SOLUTION OF THE FINITE DIFFERENCE EQ.
434      C OF THE CONVECTION-DISPERSION AND MULTIREACTION SYSTEM
435      C *****
436      C
437      C SUBROUTINE SMRTM
438      C IMPLICIT REAL*8(A-H,O-Z)
439      C COMMON/L1/ C (101),DC (101),DU (101),DL (101),E (101),S1 (101),S2 (101)
440      C COMMON/L2/ SIR (101),CX (101),S1X (101),S2X (101)
441      C COMMON/L3/ X (101),S3 (101),S3X (101)
442      C COMMON/L4/ TH,ROU,COL,WFLX,CI,CS,D,K1,K2,W,K3,K4,U,KS,K5,K6,KD
443      C COMMON/L5/ NEQ,IT,N,NM1,NP1

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433      COMMON/L6/ TPULSE, TTOTAL, TPRINT, DT, DX, GAMMA, BETA
434      REAL*8 K1, K2, K3, K4, K5, K6, KS, KD, NEQ
435      C
436      C
437      FF=2*DX
438      PV=WFLX/TH
439      RS=NEQ*ROU*KD/TH
440      C(1)=(WFLX*FF*CS+D*TH*C(3))/(WFLX*FF+D*TH)
441      DO 35 IJ=1, IT
442      M=2
443      DO 10 I=1, NM1
444      DC(I)=1.0D0+2.0D0*GAMMA*D-BETA*PV
445      DU(I)=BETA*PV-GAMMA*D
446      E(I)=C(M)+GAMMA*D*(C(M+1)-2.0D0*C(M)+C(M-1))
447      DL(I)=-GAMMA*D
448      M=I+2
449      10 CONTINUE
450      M=N
451      DC(NM1)=1.0D0+GAMMA*D
452      E(1)=E(1)+GAMMA*D*C(1)
453      C
454      C      INCORPORATION OF NONLINEAR KINETIC AND EQUILIBRIUM PROCESSES
455      C      (REVERSIBLE) IN MAIN DIAGONAL ELEMENTS AND RHS VECTOR
456      C
457      DO 20 I=1, NM1
458      DC(I)=DC(I)+DT*KS/2
459      R=0.0D0
460      H1=0.0D0
461      H2=0.0D0
462      IF((C(I+1).LT.1.0D-4).OR.(CX(I+1).LE.1.0D-4)) GO TO 15
463      R=RS*(0.50D0*(C(I+1)+CX(I+1)))*(NEQ-1.0D0)
464      H1=(0.50D0*(C(I+1)+CX(I+1)))*W
465      H2=(0.50D0*(C(I+1)+CX(I+1)))*U
466      15 DC(I)=DC(I)+R
467      E(I)=E(I)-DT*(K1*H1-K2*(ROU/TH)*(S1(I+1)+S1X(I+1))/2)
468      &-DT*(K3*H2-K4*(ROU/TH)*(S2(I+1)+S2X(I+1))/2)
469      20 E(I)=E(I)+C(I+1)*R-DT*(KS/2)*((C(I+1)+CX(I+1))/2)
470      C
471      CALL TRIDM(DC, DU, DL, E, NM1)
472      DO 25 I=2, N
473      CX(I)=E(I-1)
474      25 CX(NP1)=CX(N)
475      CX(1)=C(1)
476      DO 30 I=1, NP1
477      H1=0.0D0
478      H2=0.0D0
479      IF(C(I).GT.1.0D-4) H1=((C(I)+CX(I))/2)*W
480      IF(C(I).GT.1.0D-4) H2=((C(I)+CX(I))/2)*U
481      S1X(I)=S1(I)+DT*(K1*(TH/ROU)*H1-K2*(S1(I)+S1X(I))/2)
482      S2X(I)=S2(I)+DT*K3*(TH/ROU)*H2-(K4+K5)*DT*(S2(I)+S2X(I))/2
483      S3(I)=S3(I)+DT*K6*S3(I)
484      30 CONTINUE
485      35 CONTINUE
486      C
487      C
488      DO 50 I=1, NP1
489      C(I)=CX(I)
490      S1(I)=S1X(I)
491      S2(I)=S2X(I)
492      S3(I)=S3(I)+DT*K5*S2(I)
493      S3(I)=S3(I)-DT*K6*S3(I)
494      50 SIR(I)=SIR(I)+DT*KS*(TH/ROU)*C(I)
495      RETURN
496      END
497      C
498      C
499      C      SUBROUTINE TRIDM GIVES A SOLUTION OF A TRIDIAGONAL MATRIX-VECTOR
500      C      EQUATION USING THOMAS ALGORITHM
501      C
502      C
503      SUBROUTINE TRIDM(A,B,C,D,N)
504      IMPLICIT REAL*8(A-H,O-Z)
505      DIMENSION A(N), B(N), C(N), D(N)
506      DO 1 I=2, N
507      C(I)=C(I)/A(I-1)
508      A(I)=A(I)-(C(I)*B(I-1))

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509      1 CONTINUE
510      DO 2 I=2,N
511      D(I)=D(I)-(C(I)*D(I-1))
512      2 CONTINUE
513      D(N)=D(N)/A(N)
514      DO 3 I=2,N
515      D(N+1-I)=(D(N+1-I)-(B(N+1-I)*D(N+2-I)))/A(N+1-I)
516      3 CONTINUE
517      RETURN
518      END
519  C
520  C *****
521  C SUBROUTINE INTEG PERFORMS INTEGRATION OF A TABULAR FUNCTION Y
522  C GIVEN AT EQUAL DISTANCES H USING TRAPEZOIDAL RULE.
523  C *****
524  C
525      SUBROUTINE INTEG(H,Y,Z,N)
526      IMPLICIT REAL*8(A-H,O-Z)
527      DIMENSION Y(N),Z(N)
528      S2=0.0D0
529      IF(N-1) 40,30,10
530      10 HH=H/2.0D0
531      DO 20 I =2,N
532      S1=S2
533      S2=S2+HH*(Y(I)+Y(I-1))
534      20 Z(I-1)=S1
535      30 Z(N)=S2
536      40 RETURN
537      END

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Sample of MRTM Input Data

1. MOISTURE CONTENT,CM3/CM3	(TH) =	0.400E00
2. BULK DENSITY,G/CM3	(ROU) =	1.250E00
3. COLUMN LENGTH,CM	(COL) =	10.000E00
4. WATER FLUX,CM/HR	(WFLX) =	1.000E00
5. INITIAL CONCENTRATION,MG/L	(CI) =	0.000E00
6. CONCEN.IN INPUT PULSE,MG/L	(CS) =	10.000E00
7. DISPERSION COEFFICIENT,D,CM2/HR	(D) =	1.000E00
8. DISTRIB. COEFF. FOR EQL. SORP,CM3/G	(KD) =	1.000E00
9. NONLINEAR PARAM.FOR EQL. MECH.	(NEQ) =	1.000E00
10. FORWARD RATE REACTION, K1,HR-1	(K1) =	0.100E00
11. BACKWARD RATE REACTION, K2,HR-1	(K2) =	0.100E00
12. NONLINEAR KINETIC PARAMETER, W,	(W) =	0.500E00
13. FORWARD RATE REACTION, K3,HR-1	(K3) =	0.000E00
14. BACKWARD RATE REACTION, K4,HR-1	(K4) =	0.000E00
15. NONLINEAR KINETIC PARAMETER, U,	(U) =	0.000E00
16. IRREVERSIBLE REACTION RATE,KS,HR-1	(KS) =	0.000E00
17. FORWARD RATE REACTION, K5,HR-1	(K5) =	0.000E00
18. BACKWARD RATE REACTION, K6,HR-1	(K6) =	0.000E00
19. NUMBER OF ITERATIONS (M)	(IT) =	000
20. INPUT PULSE DURATION,HR	(TPULSE) =	12.000E00
21. TOTAL SIMULATION TIME,HR	(TTOTAL) =	16.000E00
22. PRINTOUT TIME DESIRED,HR	(TPRINT) =	4.000E00
23. INCREMENTAL TIME STEP,HR	(DT) =	0.200E00
24. INCREMENTAL DEPTH, CM	(DX) =	1.000E00

MRTM Computer Program Output Listing

M. R. T. M.

SIMULATION RESULTS USING MRTM MODEL FOR TRANSPORT

AND

RETENTION OF HEAVY METALS IN THE SOIL

UNDER

STEADY WATER FLOW CONDITIONS

PROGRAM WRITTEN AND DOCUMENTED

by

H. M. SELIM

April 1990

INPUT PARAMETERS :

1.	MOISTURE CONTENT, CM3/CM3	(TH)	=	.40000
2.	BULK DENSITY, G/CM3	(ROU)	=	1.25000
3.	COLUMN LENGTH, CM	(COL)	=	10.00000
4.	WATER FLUX, CM/HOUR	(WFLX)	=	1.00000
5.	INITIAL CONCENTRATION, MG/L	(CI)	=	.00000
6.	CONCEN. IN INPUT PULSE, MG/L	(CS)	=	10.00000
7.	DISPERSION COEFFICIENT, CM2/HR	(D)	=	1.00000
8.	FORWARD RATE REACTION, K1, HR-1	(K1)	=	.10000
9.	BACKWARD RATE REACTION, K2, HR-1	(K2)	=	.10000
10.	NONLINEAR KINETIC PARAMETER, W,	(W)	=	.00000
11.	FORWARD RATE REACTION, K3, HR-1	(K3)	=	.00000
12.	BACKWARD RATE REACTION, K4, HR-1	(K4)	=	.00000
13.	NONLINEAR KINETIC PARAMETER, U,	(U)	=	.50000
14.	IRREVERSIBLE REACTION RATE, KS, HR-1	(KS)	=	.00000
15.	FORWARD RATE REACTION, K5, HR-1	(K5)	=	.00000
16.	BACKWARD RATE REACTION, K6, HR-1	(K6)	=	.00000
17.	NUMBER OF ITERATIONS	(IT)	=	0
18.	DISTRIBUTION COEFFICIENT FOR EQUILIBRIUM SORPTION, KD, CM3/G	(KD)	=	1.00000
19.	NONLINEAR PARAMETER FOR EQUILIBRIUM MECHANISM, NEQ	(NEQ)	=	1.00000
20.	INPUT PULSE DURATION, HR	(TPULSE)	=	12.00000
21.	TOTAL SIMULATION TIME, HR	(TTOTAL)	=	16.00000
22.	PRINTOUT TIME DESIRED, HR	(TPRINT)	=	4.00000

THE INCREMENTS USED WERE :

1.	SIMULATION DEPTH INTERVAL, CM	(DX)	=	.25000
2.	INCREMENTAL TIME STEP, HR	(DT)	=	.02000

S I M U L A T I O N T I M E (HOUR) = 4.00

PORE VOLUMES (V/V0) = 1.00 REL. CONCENTRATION (C/C0) = .0000

CONCENTRATION DISTRIBUTION

DEPTH	SOLUT	EQUIL	KINETIC	KINETIC	KINETIC	IRREV.	TOTAL
X	CONC.	PHASE	PHASE 1	PHASE 2	PHASE 3	SINK	SORBED
	C	SE	S1	S2	S3	SIR	S
CM	--MG/L--						
.00	9.6609	9.6609	.309	.000	.000	.000	9.970
.25	9.4858	9.4858	.292	.000	.000	.000	9.778
.50	9.2452	9.2452	.271	.000	.000	.000	9.517
.75	8.9264	8.9264	.249	.000	.000	.000	9.176
1.00	8.5172	8.5172	.227	.000	.000	.000	8.744
1.25	8.0103	8.0103	.204	.000	.000	.000	8.214
1.50	7.4062	7.4062	.181	.000	.000	.000	7.587
1.75	6.7150	6.7150	.159	.000	.000	.000	6.874
2.00	5.9561	5.9561	.138	.000	.000	.000	6.094
2.25	5.1573	5.1573	.119	.000	.000	.000	5.276
2.50	4.3512	4.3512	.101	.000	.000	.000	4.452
2.75	3.5713	3.5713	.084	.000	.000	.000	3.655
3.00	2.8478	2.8478	.069	.000	.000	.000	2.917
3.25	2.2038	2.2038	.057	.000	.000	.000	2.260
3.50	1.6536	1.6536	.045	.000	.000	.000	1.699
3.75	1.2021	1.2021	.036	.000	.000	.000	1.238
4.00	.8462	.8462	.028	.000	.000	.000	.874
4.25	.5763	.5763	.022	.000	.000	.000	.598
4.50	.3796	.3796	.016	.000	.000	.000	.396
4.75	.2416	.2416	.012	.000	.000	.000	.254
5.00	.1484	.1484	.009	.000	.000	.000	.157
5.25	.0879	.0879	.006	.000	.000	.000	.094
5.50	.0500	.0500	.004	.000	.000	.000	.054
5.75	.0273	.0273	.003	.000	.000	.000	.030
6.00	.0142	.0142	.002	.000	.000	.000	.016
6.25	.0071	.0071	.001	.000	.000	.000	.008
6.50	.0033	.0033	.001	.000	.000	.000	.004
6.75	.0014	.0014	.001	.000	.000	.000	.002
7.00	.0006	.0006	.000	.000	.000	.000	.001
7.25	.0002	.0002	.000	.000	.000	.000	.000
7.50	.0001	.0001	.000	.000	.000	.000	.000
7.75	.0001	.0001	.000	.000	.000	.000	.000
8.00	.0001	.0001	.000	.000	.000	.000	.000
8.25	.0001	.0001	.000	.000	.000	.000	.000
8.50	.0001	.0001	.000	.000	.000	.000	.000
8.75	.0001	.0001	.000	.000	.000	.000	.000
9.00	.0001	.0001	.000	.000	.000	.000	.000
9.25	.0001	.0001	.000	.000	.000	.000	.000
9.50	.0001	.0001	.000	.000	.000	.000	.000
9.75	.0001	.0001	.000	.000	.000	.000	.000
10.00	.0001	.0001	.000	.000	.000	.000	.000

S A L T B A L A N C E :

TOTAL INPUT SOLUTE FROM PULSE	(MG)	=	40.0000
TOTAL SOLUTE SOIL SOLUTION PHASE	(MG)	=	9.2465
TOTAL SORBED IN (EQUILIB) PHASE SE	(MG)	=	28.8953
TOTAL SORBED IN (KINETIC) PHASE S1	(MG)	=	.7791
TOTAL SORBED IN (KINETIC) PHASE S2	(MG)	=	.0000
TOTAL SORBED IN (KINETIC) PHASE S3	(MG)	=	.0000
TOTAL SORBED IN IRREVERSIBLE PHASE	(MG)	=	.0000
TOTAL SOLUTE IN THE EFFLUENT	(MG)	=	.0001
MASS BALANCE (CALC.OUTPUT/INPUT)	()	=	97.3025

S I M U L A T I O N T I M E (HOUR) = 8.00

PORE VOLUMES (V/V0) = 2.00 REL. CONCENTRATION (C/C0) = .0013

CONCENTRATION DISTRIBUTION

DEPTH	SOLUT	EQUIL	KINETIC	KINETIC	KINETIC	IRREV.	TOTAL
X	CONC.	PHASE	PHASE 1	PHASE 2	PHASE 3	SINK	SORBED
CM	--MG/L--	SE	S1	S2	S3	SIR	S
1.00	9.9432	9.9432	.539	.000	.000	.000	10.482
1.25	9.9120	9.9120	.526	.000	.000	.000	10.438
1.50	9.8730	9.8730	.511	.000	.000	.000	10.384
1.75	9.8242	9.8242	.494	.000	.000	.000	10.318
2.00	9.7623	9.7623	.475	.000	.000	.000	10.238
2.25	9.6836	9.6836	.456	.000	.000	.000	10.140
2.50	9.5836	9.5836	.436	.000	.000	.000	10.020
2.75	9.4575	9.4575	.416	.000	.000	.000	9.873
3.00	9.2998	9.2998	.395	.000	.000	.000	9.694
3.25	9.1050	9.1050	.373	.000	.000	.000	9.478
3.50	8.8682	8.8682	.351	.000	.000	.000	9.219
3.75	8.5850	8.5850	.329	.000	.000	.000	8.914
4.00	8.2524	8.2524	.306	.000	.000	.000	8.559
4.25	7.8693	7.8693	.284	.000	.000	.000	8.153
4.50	7.4370	7.4370	.262	.000	.000	.000	7.699
4.75	6.9589	6.9589	.240	.000	.000	.000	7.199
5.00	6.4412	6.4412	.219	.000	.000	.000	6.660
5.25	5.8926	5.8926	.198	.000	.000	.000	6.091
5.50	5.3235	5.3235	.178	.000	.000	.000	5.502
5.75	4.7459	4.7459	.159	.000	.000	.000	4.905
6.00	4.1721	4.1721	.141	.000	.000	.000	4.314
6.25	3.6144	3.6144	.125	.000	.000	.000	3.739
6.50	3.0838	3.0838	.109	.000	.000	.000	3.193
6.75	2.5900	2.5900	.095	.000	.000	.000	2.685
7.00	2.1401	2.1401	.082	.000	.000	.000	2.222
7.25	1.7390	1.7390	.070	.000	.000	.000	1.809
7.50	1.3889	1.3889	.059	.000	.000	.000	1.448
7.75	1.0898	1.0898	.050	.000	.000	.000	1.139
8.00	.8398	.8398	.041	.000	.000	.000	.881
8.25	.6351	.6351	.034	.000	.000	.000	.669
8.50	.4712	.4712	.028	.000	.000	.000	.499
8.75	.3427	.3427	.022	.000	.000	.000	.365
9.00	.2441	.2441	.018	.000	.000	.000	.262
9.25	.1702	.1702	.014	.000	.000	.000	.184
9.50	.1159	.1159	.011	.000	.000	.000	.127
9.75	.0771	.0771	.008	.000	.000	.000	.086
10.00	.0499	.0499	.006	.000	.000	.000	.056
	.0314	.0314	.005	.000	.000	.000	.036
	.0194	.0194	.004	.000	.000	.000	.023
	.0126	.0126	.003	.000	.000	.000	.015
	.0126	.0126	.003	.000	.000	.000	.015

S A L T B A L A N C E :

TOTAL INPUT SOLUTE FROM PULSE (MG) = 80.0000
TOTAL SOLUTE SOIL SOLUTION PHASE (MG) = 19.4680
TOTAL SORBED IN (EQUILIB) PHASE SE (MG) = 57.7125
TOTAL SORBED IN (KINETIC) PHASE S1 (MG) = 2.4389
TOTAL SORBED IN (KINETIC) PHASE S2 (MG) = .0000
TOTAL SORBED IN (KINETIC) PHASE S3 (MG) = .0000
TOTAL SORBED IN IRREVERSIBLE PHASE (MG) = .0000
TOTAL SOLUTE IN THE EFFLUENT (MG) = .0060
MASS BALANCE (CALC.OUTPUT/INPUT) () = 98.2818

S I M U L A T I O N T I M E (HOUR) = 12.00

PORE VOLUMES (V/V0) = 3.00 REL. CONCENTRATION (C/C0) = .0987

CONCENTRATION DISTRIBUTION

DEPTH	SOLUT	EQUIL	KINETIC	KINETIC	KINETIC	IRREV.	TOTAL
X	CONC.	PHASE	PHASE 1	PHASE 2	PHASE 3	SINK	SORBED
	C	SE	S1	S2	S3	SIR	S
CM	--MG/L--						
.00	4.4218	4.4218	.694	.000	.000	.000	5.116
.25	9.5454	9.5454	.685	.000	.000	.000	10.231
.50	9.9334	9.9334	.675	.000	.000	.000	10.608
.75	9.9319	9.9319	.663	.000	.000	.000	10.595
1.00	9.9135	9.9135	.650	.000	.000	.000	10.564
1.25	9.8917	9.8917	.637	.000	.000	.000	10.528
1.50	9.8663	9.8663	.623	.000	.000	.000	10.489
1.75	9.8365	9.8365	.608	.000	.000	.000	10.444
2.00	9.8011	9.8011	.592	.000	.000	.000	10.393
2.25	9.7586	9.7586	.576	.000	.000	.000	10.335
2.50	9.7075	9.7075	.560	.000	.000	.000	10.267
2.75	9.6457	9.6457	.542	.000	.000	.000	10.188
3.00	9.5709	9.5709	.524	.000	.000	.000	10.095
3.25	9.4805	9.4805	.506	.000	.000	.000	9.987
3.50	9.3719	9.3719	.487	.000	.000	.000	9.859
3.75	9.2420	9.2420	.468	.000	.000	.000	9.709
4.00	9.0878	9.0878	.448	.000	.000	.000	9.535
4.25	8.9067	8.9067	.427	.000	.000	.000	9.334
4.50	8.6959	8.6959	.407	.000	.000	.000	9.103
4.75	8.4535	8.4535	.386	.000	.000	.000	8.839
5.00	8.1780	8.1780	.365	.000	.000	.000	8.543
5.25	7.8689	7.8689	.344	.000	.000	.000	8.213
5.50	7.5267	7.5267	.323	.000	.000	.000	7.849
5.75	7.1530	7.1530	.302	.000	.000	.000	7.455
6.00	6.7503	6.7503	.281	.000	.000	.000	7.031
6.25	6.3227	6.3227	.261	.000	.000	.000	6.583
6.50	5.8749	5.8749	.241	.000	.000	.000	6.115
6.75	5.4127	5.4127	.221	.000	.000	.000	5.634
7.00	4.9425	4.9425	.202	.000	.000	.000	5.145
7.25	4.4711	4.4711	.184	.000	.000	.000	4.655
7.50	4.0054	4.0054	.167	.000	.000	.000	4.172
7.75	3.5519	3.5519	.151	.000	.000	.000	3.702
8.00	3.1168	3.1168	.135	.000	.000	.000	3.252
8.25	2.7055	2.7055	.120	.000	.000	.000	2.826
8.50	2.3224	2.3224	.107	.000	.000	.000	2.429
8.75	1.9711	1.9711	.094	.000	.000	.000	2.065
9.00	1.6544	1.6544	.083	.000	.000	.000	1.737
9.25	1.3761	1.3761	.072	.000	.000	.000	1.448
9.50	1.1447	1.1447	.063	.000	.000	.000	1.208
9.75	.9866	.9866	.056	.000	.000	.000	1.043
10.00	.9866	.9866	.056	.000	.000	.000	1.043

S A L T B A L A N C E :

TOTAL INPUT SOLUTE FROM PULSE	(MG)	=	120.0000
TOTAL SOLUTE SOIL SOLUTION PHASE	(MG)	=	27.0681
TOTAL SORBED IN (EQUILIB) PHASE SE	(MG)	=	84.5877
TOTAL SORBED IN (KINETIC) PHASE S1	(MG)	=	4.5650
TOTAL SORBED IN (KINETIC) PHASE S2	(MG)	=	.0000
TOTAL SORBED IN (KINETIC) PHASE S3	(MG)	=	.0000
TOTAL SORBED IN IRREVERSIBLE PHASE	(MG)	=	.0000
TOTAL SOLUTE IN THE EFFLUENT	(MG)	=	1.2313
MASS BALANCE (CALC.OUTPUT/INPUT)	()	=	97.8768

S I M U L A T I O N T I M E (HOUR) = 16.00

PORE VOLUMES (V/V0) = 4.00 REL. CONCENTRATION (C/C0) = .4478

CONCENTRATION DISTRIBUTION

DEPTH	SOLUT	EQUIL	KINETIC	KINETIC	KINETIC	IRREV.	TOTAL
X	CONC.	PHASE	PHASE 1	PHASE 2	PHASE 3	SINK	SORBED
	C	SE	S1	S2	S3	SIR	S
CM	--MG/L--						
.00	.3245	.3245	.581	.000	.000	.000	.905
.25	.4905	.4905	.605	.000	.000	.000	1.095
.50	.7217	.7217	.625	.000	.000	.000	1.347
.75	1.0310	1.0310	.643	.000	.000	.000	1.674
1.00	1.4309	1.4309	.657	.000	.000	.000	2.088
1.25	1.9284	1.9284	.668	.000	.000	.000	2.596
1.50	2.5230	2.5230	.676	.000	.000	.000	3.199
1.75	3.2040	3.2040	.681	.000	.000	.000	3.885
2.00	3.9513	3.9513	.684	.000	.000	.000	4.635
2.25	4.7362	4.7362	.683	.000	.000	.000	5.419
2.50	5.5252	5.5252	.680	.000	.000	.000	6.205
2.75	6.2841	6.2841	.675	.000	.000	.000	6.959
3.00	6.9823	6.9823	.668	.000	.000	.000	7.650
3.25	7.5964	7.5964	.658	.000	.000	.000	8.255
3.50	8.1118	8.1118	.648	.000	.000	.000	8.759
3.75	8.5233	8.5233	.636	.000	.000	.000	9.159
4.00	8.8337	8.8337	.622	.000	.000	.000	9.456
4.25	9.0515	9.0515	.608	.000	.000	.000	9.660
4.50	9.1887	9.1887	.593	.000	.000	.000	9.782
4.75	9.2581	9.2581	.577	.000	.000	.000	9.835
5.00	9.2719	9.2719	.561	.000	.000	.000	9.832
5.25	9.2402	9.2402	.543	.000	.000	.000	9.784
5.50	9.1710	9.1710	.526	.000	.000	.000	9.697
5.75	9.0697	9.0697	.508	.000	.000	.000	9.577
6.00	8.9398	8.9398	.489	.000	.000	.000	9.429
6.25	8.7831	8.7831	.470	.000	.000	.000	9.253
6.50	8.6007	8.6007	.451	.000	.000	.000	9.052
6.75	8.3925	8.3925	.431	.000	.000	.000	8.824
7.00	8.1587	8.1587	.412	.000	.000	.000	8.570
7.25	7.8993	7.8993	.392	.000	.000	.000	8.291
7.50	7.6148	7.6148	.372	.000	.000	.000	7.987
7.75	7.3059	7.3059	.352	.000	.000	.000	7.658
8.00	6.9743	6.9743	.332	.000	.000	.000	7.306
8.25	6.6219	6.6219	.312	.000	.000	.000	6.934
8.50	6.2518	6.2518	.293	.000	.000	.000	6.545
8.75	5.8683	5.8683	.273	.000	.000	.000	6.142
9.00	5.4777	5.4777	.255	.000	.000	.000	5.732
9.25	5.0921	5.0921	.237	.000	.000	.000	5.329
9.50	4.7374	4.7374	.221	.000	.000	.000	4.958
9.75	4.4777	4.4777	.208	.000	.000	.000	4.686
10.00	4.4777	4.4777	.208	.000	.000	.000	4.686

S A L T B A L A N C E :

TOTAL INPUT SOLUTE FROM PULSE	(MG)	=	120.0000
TOTAL SOLUTE SOIL SOLUTION PHASE	(MG)	=	24.9722
TOTAL SORBED IN (EQUILIB) PHASE SE	(MG)	=	78.0380
TOTAL SORBED IN (KINETIC) PHASE S1	(MG)	=	6.3496
TOTAL SORBED IN (KINETIC) PHASE S2	(MG)	=	.0000
TOTAL SORBED IN (KINETIC) PHASE S3	(MG)	=	.0000
TOTAL SORBED IN IRREVERSIBLE PHASE	(MG)	=	.0000
TOTAL SOLUTE IN THE EFFLUENT	(MG)	=	11.6760
MASS BALANCE (CALC.OUTPUT/INPUT)	(%)	=	100.8631

APPENDIX C: SOTS MODEL

Computer Program Listing

```

1      C
2      $LARGE
3      C*****
4      C
5      C                      S O T S                      C
6      C
7      C*****
8      C
9      C  NUMERICAL SOLUTION OF THE SOLUTE CONVECTIVE - DISPERSIVE EQUATIONS  C
10     C
11     C          UNDER STEADY-STATE WATER FLUX CONDITIONS          C
12     C
13     C                      W I T H                      C
14     C
15     C          SECOND-ORDER TWO-SITE REACTIONS                    C
16     C
17     C*****
18     C          PROGRAM WRITTEN AND DOCUMENTED BY                  C
19     C
20     C                      by                      C
21     C
22     C                      H. M. SELIM                      C
23     C                      February 1990                      C
24     C*****
25     C
26     C      IMPLICIT REAL*8 (A-H,O-Z)
27     C      DIMENSION C(501),DC(501),DU(501),DL(501),E(501),S1(501),S2(501)
28     C      DIMENSION SIR(501),CX(501),S1X(501),S2X(501),S3(501),S3X(501)
29     C      DIMENSION SC1(501),SC1X(501),SC2(501),SC2X(501)
30     C      DIMENSION X(501)
31     C      CHARACTER*64 FNAME1,FNAMEO
32     C      CHARACTER*64 USER,SOIL,SOLUTE,DATE
33     C      REAL*8 K1,K2,K3,K4,KS
34     C      REAL*8 KAPPA1,KAPPA2,KAPPA3,KAPPA4,KAPPAS
35     C
36     C
37     C      WRITE(*,100)
38     C  --- READ INPUT PARAMETERS -----
39     C
40     C      WRITE(*,*) ' PLEASE ENTER USER NAME (OPTIONAL):'
41     C      READ(*,800) USER
42     C      WRITE(*,*) ' PLEASE ENTER NAME OF SOIL (OPTIONAL):'
43     C      READ(*,800) SOIL
44     C      WRITE(*,*) ' PLEASE ENTER NAME OF SOLUTE (OPTIONAL):'
45     C      READ(*,800) SOLUTE
46     C      WRITE(*,*) ' ENTER DATE OR OTHER IDENTIFICATION (OPTIONAL):'
47     C      READ(*,800) DATE
48     C      WRITE(*,*) ' '
49     C      WRITE(*,*)
50     C      $' ----- INPUT PARAMETERS SECTION -----'
51     C      WRITE(*,*) ' '
52     C      WRITE(*,*) ' INPUT PARAMETERS CAN BE PROVIDED IN TWO WAYS;'
53     C      WRITE(*,*) ' ENTER 1 if you wish to enter the input data using'
54     C      WRITE(*,*) ' the keyboard (i.e. interactively)'
55     C      WRITE(*,*) ' '
56     C      WRITE(*,*) ' OR'
57     C      WRITE(*,*) ' '
58     C      WRITE(*,*) ' ENTER 2 if an input data file is to be provided'
59     C      WRITE(*,*)
60     C      $' PLEASE ENTER EITHER 1 OR 2'
61     C      READ(*,950) IFLAG
62     C      IF(IFLAG.NE.1) THEN
63     C      WRITE(*,'(A)') ' PLEASE ENTER NAME OF INPUT FILE?'
64     C      WRITE(*,*) '(for example A:XX.DAT or C:UU.DAT for hard disk)'

```

```

65      READ(*,'(A)') FNAMEI
66      OPEN(5,FILE=FNAMEI)
67      C
68      READ(5,700) TH,ROU,COL,WFLX
69      READ(5,700) CI,CS,D,ST,F
70      READ(5,700) K1,K2
71      READ(5,700) K3,K4
72      READ(5,700) KS
73      READ(5,750) IT
74      READ(5,700) TPULSE,TTOTAL,TPRINT,DT,DX
75      C
76      ELSE
77      C
78      WRITE(*,*)
79      $'PLEASE ENTER THE FOLLOWING INPUT PARAMETERS : '
80      WRITE(*,*) ' '
81      WRITE(*,*)
82      $' (1) MOISTURE CONTENT,CM3/CM3 (TH) ='
83      WRITE(*,*)
84      $'(Values usually less than 0.65 cm3/cm3). Enter your value NOW'
85      READ(*,900) TH
86      WRITE(*,*)
87      $' (2) BULK DENSITY,G/CM3 (ROU) ='
88      WRITE(*,*)
89      $'(Range of values 1.1 - 1.7 g/cm3). Enter your value NOW'
90      READ(*,900) ROU
91      WRITE(*,*)
92      $' (3) COLUMN LENGTH (CM) (COL) ='
93      READ(*,900) COL
94      WRITE(*,*)
95      $' (4) WATER FLUX (CM/HR) (WFLX) ='
96      WRITE(*,*)
97      $'(Range of values 0.01 - 5 cm/hr). Enter your value NOW'
98      READ(*,900) WFLX
99      WRITE(*,*)
100     $' (5) INITIAL CONCENTRATION, (CI) ='
101     READ(*,900) CI
102     WRITE(*,*)
103     $' (6) APPLIED CONCENTRATION, (CS) ='
104     READ(*,900) CS
105     WRITE(*,*)
106     $' (7) DISPERSION COEFFICIENT, (CM2/HR) (D) ='
107     WRITE(*,*) $'(Ranges from .1 - 1.5 CM2/HR). Enter your value NOW'
108     READ(*,900) D
109     WRITE(*,*)
110     $' (8) TOTAL SORPTION SITES (ST) ='
111     WRITE(*,*) $'(Ranges from 200 to 2000 mg/kg). Enter your value NOW'
112     READ(*,900) ST
113     WRITE(*,*)
114     $' (9) FRACTION OF SITES, F (F) ='
115     WRITE(*,*) $'(Ranges from 0.0 to 1.0). Enter your value NOW'
116     READ(*,900) F
117     WRITE(*,*)
118     $' (10) FORWARD RATE REACTION, K1,HR-1 (K1) ='
119     WRITE(*,*) $'(Ranges from 0.001-0.1 hr-1). Enter your value NOW'
120     READ(*,900) K1
121     WRITE(*,*)
122     $' (11) BACKWARD RATE REACTION, K2,HR-1 (K2) ='
123     WRITE(*,*) $'(Ranges from 0.01 - 0.5 hr-1). Enter your value NOW'
124     READ(*,900) K2
125     WRITE(*,*)
126     $' (12) FORWARD RATE REACTION, K3,HR-1 (K3) ='
127     WRITE(*,*) $'(Ranges 0.0001 - 0.05 hr-1). Enter your value NOW'
128     READ(*,900) K3
129     WRITE(*,*)
130     $' (13) BACKWARD RATE REACTION, K4,HR-1 (K4) ='
131     WRITE(*,*) $'(Ranges from 0.05 - 5. hr-1). Enter your value NOW'
132     READ(*,900) K4
133     WRITE(*,*)
134     $' (14) IRREVERSIBLE REACTION RATE,KS,HR-1 (KS) ='

```

```

135      WRITE(*,*) '(Range is 0.0001 - 0.5 hr-1). Enter your value NOW'
136      READ(*,900) KS
137      WRITE(*,*)
138      $' (15) NUMBER OF ITERATIONS (IT) (integer value from 0 to 9) '
139      READ(*,950) IT
140      WRITE(*,*)
141      $' (16) INPUT PULSE DURATION, HR      (TPULSE)  ='
142      READ(*,900) TPULSE
143      WRITE(*,*)
144      $' (17) TOTAL SIMULATION TIME,HR      (TTOTAL)  ='
145      READ(*,900) TTOTAL
146      WRITE(*,*)
147      $' (18) PRINTOUT TIME DESIRED,HR      (TPRINT)  ='
148      READ(*,900) TPRINT
149      WRITE(*,*)
150      $' (19) INCREMENTAL DISTANCE, CM      (DX)      ='
151      WRITE(*,*)
152      $'      A default value of DX=1.00 is given      '
153      READ(*,900) DDX
154      WRITE(*,*)
155      $' (20) INCREMENTAL TIME STEP,HR      (DT)      ='
156      WRITE(*,*)
157      $'      A default value of Dt=0.02 is given      '
158      READ(*,900) DDT
159      ENDIF
160      C
161      XIN=1.00
162      IF(DDX.NE.0.0) THEN
163      DX=DDX
164      ELSE
165      DX=XIN
166      ENDIF
167      PIN=0.02
168      IF(DDT.NE.0.0) THEN
169      DT=DDT
170      ELSE
171      DT=PIN
172      ENDIF
173      C
174      WRITE(*,'(A)') '      PLEASE ENTER NAME OF OUTPUT FILE (FOR EXAMPLE
175      * B:ZZ.DAT)'
176      READ(*,'(A)') FNAMEO
177      OPEN(6,FILE=FNAMEO,STATUS='UNKNOWN')
178      C
179      C-----Write Title Heading -----
180      WRITE(6,100)
181      WRITE(6,800) USER
182      WRITE(6,800) SOIL
183      WRITE(6,800) SOLUTE
184      WRITE(6,800) DATE
185      WRITE(6,300) TH,ROU,COL,WFLX,CI,CS,D,K1,K2,K3,K4,F,ST,KS
186      WRITE(6,310) IT,TPULSE,TTOTAL,TPRINT
187      C
188      PV=WFLX/TH
189      RS=NEQ*ROU*KD/TH
190      CO=CS
191      EF=0.0D0
192      TIME=0.0D0
193      5  CONTINUE
194      GAMMA=DT/(2.D0*DX*DX)
195      BETA=DT/DX
196      IF((BETA*PV).GT.0.50D0) GO TO 7
197      IF((GAMMA*D/(BETA*PV)).LT.0.50D0) GO TO 6
198      GO TO 8
199      6  DX=DX/2
200      GO TO 5
201      7  DT=DT/2
202      GO TO 5
203      8  CONTINUE
204      N=COL/DX

```



```

205      NM1=N-1
206      NM2=N-2
207      NP1=N+1
208      GAMMA=DT/(2*DX*DX)
209      BETA=DT/DX
210      WRITE(6,400) DX,DT
211      IF(N.LT.500) GO TO 9
212      WRITE(*,*) ' W A R N I N G '
213      WRITE(*,*)
214      &'Dimension of variables exceed 500. Did you increase array sizes'
215      WRITE(*,*)
216      &' If not, the program will terminate abruptly (see text).'
217      9  CONTINUE
218      C
219      KAPPA1=K1*TH*TH*COL*CS/(ROU*WFLX)
220      KAPPA2=K2*TH*COL/WFLX
221      KAPPA3=K3*TH*TH*COL*CS/(ROU*WFLX)
222      KAPPA4=K4*TH*COL/WFLX
223      KAPPAS=KS*TH*COL/WFLX
224      OMEGA=ST*ROU/(CS*TH)
225      PE=WFLX*COL/(TH*D)
226      WRITE(6,340) KAPPA1,KAPPA2,KAPPA3,KAPPA4,KAPPAS,BETTA,PE
227      C
228      DO 10 I=1,NP1
229      SIR(I)=0.0D0
230      S1(I)=F*ST
231      S2(I)=(1.0D0-F)*ST
232      S1X(I)=S1(I)
233      S2X(I)=S2(I)
234      SC1(I)=0.0D0
235      SC2(I)=0.0D0
236      SC1X(I)=0.0D0
237      SC2X(I)=0.0D0
238      CX(I)=CI
239      10  C(I)=CI
240      FF=2*DX
241      NKK=TPRINT/DT+0.50D0
242      KLM=TTOTAL/DT+0.50D0
243      KK=KLM/NKK+0.5D0
244      C
245      WRITE(*,*) '----- Initial Conditions Completed -----'
246      C
247      WRITE(*,*) '-----Execution Begins-----'
248      WRITE(*,*) '-----Please Wait-----'
249      L=0
250      IT=IT+1
251      SINT=TPULSE*CS*WFLX
252      DO 50 JJ=1,KK
253      DO 40 LL=1,NKK
254      TT=LL*DT+(JJ-1)*TPRINT
255      L=L+1
256      C
257      C(1)=(WFLX*FF*CS+D*TH*C(3))/(WFLX*FF+D*TH)
258      DO 35 IJ=1,IT
259      M=2
260      DO 15 I=1,NM1
261      DC(I)=1.0D0+2.0D0*GAMMA*I-BETA*PV
262      DU(I)=BETA*PV-GAMMA*D
263      E(I)=C(M)+GAMMA*D*(C(M+1)-2.0D0*C(M)+C(M-1))
264      DL(I)=-GAMMA*D
265      M=I+2
266      15  CONTINUE
267      M=N
268      DC(NM1)=1.0D0+GAMMA*D
269      E(1)=E(1)+GAMMA*D*C(1)
270      C
271      C  INCORPORATION OF NONLINEAR KINETIC AND EQUILIBRIUM PROCESSES
272      C  (REVERSIBLE) IN MAIN DIAGONAL ELEMENTS AND RHS VECTOR
273      C
274      C

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```

275      DO 20 I=1,NM1
276      H1=(0.50D0*(C(I+1)+CX(I+1)))*(0.50D0*(S1(I+1)+S1X(I+1)))
277      H2=(0.50D0*(C(I+1)+CX(I+1)))*(0.50D0*(S2(I+1)+S2X(I+1)))
278      E(I)=E(I)-DT*(K1*H1-K2*(ROU/TH)*(SC1(I+1)+SC1X(I+1))/2)
279      &-DT*(K3*H2-K4*(ROU/TH)*(SC2(I+1)+SC2X(I+1))/2)
280      C      DC(I)=DC(I)-DT*KS/2
281      E(I)=E(I)-DT*(KS/1)*((C(I+1)+CX(I+1))/2)
282      20  CONTINUE
283      C
284      CALL TRIDM(DC,DU,DL,E,NM1)
285      DO 25 I=2,N
286      25  CX(I)=E(I-1)
287      CX(NP1)=CX(N)
288      CX(1)=C(1)
289      DO 30 I=1,NP1
290      S1X(I)=F*ST-SC1X(I)
291      S2X(I)=(1.0D0-F)*ST-SC2X(I)
292      H1=(0.50D0*(C(I)+CX(I)))*(0.50D0*(S1(I)+S1X(I)))
293      H2=(0.50D0*(C(I)+CX(I)))*(0.50D0*(S2(I)+S2X(I)))
294      SC1X(I)=SC1(I)+DT*(K1*(TH/ROU)*H1-K2*(SC1(I)+SC1X(I))/2)
295      SC2X(I)=SC2(I)+DT*(K3*(TH/ROU)*H2-K4*(SC2(I)+SC2X(I))/2)
296      S1X(I)=F*ST-SC1X(I)
297      S2X(I)=(1-F)*ST-SC2X(I)
298      SIR(I)=SIR(I)+DT*KS*(TH/ROU)*C(I)
299      30  CONTINUE
300      35  CONTINUE
301      DO 36 I=1,NP1
302      C(I)=CX(I)
303      S1(I)=S1X(I)
304      S2(I)=S2X(I)
305      SC1(I)=SC1X(I)
306      SC2(I)=SC2X(I)
307      36  CONTINUE
308      EF=C(N)+EF
309      IF(TT.GT.TPULSE) CS=0.0D0
310      40  CONTINUE
311      TIME=JJ*TPRINT
312      C
313      C
314      WRITE(6,500) TIME
315      VV0=WFLX*TIME/(COL*TH)
316      CCO=C(N)/C0
317      WRITE(6,525) VV0,CC0
318      C
319      WRITE(*,650) TIME,VV0,CC0
320      WRITE(*,*) '-----Execution Continues-----'
321      WRITE(*,*) '-----Please Wait-----'
322      C
323      WRITE(6,550)
324      WRITE(6,560)
325      WRITE(6,570)
326      DO 45 I=1,NP1
327      DEPTH=DX*(I-1)
328      45  WRITE(6,600) DEPTH,C(I),S1(I),S2(I),SC1(I),SC2(I),SIR(I)
329      CALL INTEG(DX,C,X,NP1)
330      TSWATR=TH*X(NP1)
331      CALL INTEG(DX,SC1,X,NP1)
332      TS1=ROU*X(NP1)
333      CALL INTEG(DX,SC2,X,NP1)
334      TS2=ROU*X(NP1)
335      CALL INTEG(DX,SIR,X,NP1)
336      TSIR=ROU*X(NP1)
337      SINP=TIME*CS*WFLX
338
339      IF(SINP.GT.SINT) SINP=SINT
340      IF(CS.EQ.0.D0) SINP=SINT
341      TEFFL=EF*DT*WFLX
342      BAL=(TEFFL+TS1+TS2+TSIR+TSWATR)*100.0D0/SINP
343      WRITE(6,200) SINP,TSWATR,TS1,TS2,TSIR,TEFFL,BAL
344      50  CONTINUE

```

```

345 C
346 100 FORMAT(//,7X,
347 &'*****',
348 $//,7X,
349 &' WELCOME TO ',
350 $//,7X,
351 &' P C V E R S I O N O F ',
352 $//,7X,
353 &' SECOND - ORDER TWO - SITE MODEL ',
354 $//,7X,
355 &' S. O. T. S. ',
356 $//,7X,
357 &' SIMULATION MODEL FOR TRANSPORT ',
358 $//,7X,
359 &' AND RETENTION OF HEAVY METALS IN SOILS ',
360 $//,7X,
361 &' UNDER STEADY - STATE WATER CONDITIONS ',
362 $//,7X,
363 &'*****',
364 $/,7X,
365 &' PROGRAM WRITTEN AND DOCUMENTED ',
366 $/,7X,
367 &' by ',
368 4$//,7X,
369 &' H. M. SELIM ',
370 $/,7X,
371 &' February 1990 ',
372 $/,7X,
373 &'*****',
374 &/)
375 200 FORMAT(//,2X,'S A L T B A L A N C E :',//
376 &7X,'TOTAL INPUT SALT FROM PULSE (MG) =',F10.4,/
377 &7X,'TOTAL SALT IN SOIL SOLUTION PHASE (MG) =',F10.4,/,
378 &7X,'TOTAL SORBED IN TYPE I SITES S1 (MG) =',F10.4,/,
379 &7X,'TOTAL SORBED IN TYPE II SITES S2 (MG) =',F10.4,/,
380 &7X,'TOTAL SORBED IN IRREVERSIBLE PHASE (MG) =',F10.4,/,
381 &7X,'TOTAL SALT IN THE EFFLUENT (MG) =',F10.4,/,
382 &7X,'MASS BALANCE (CALC.OUTPUT/INPUT) (%) =',F10.4,/)
383 300 FORMAT(//,
384 $2X,'INPUT PARAMETERS :',//
385 $5X,'1. MOISTURE CONTENT, CM3/CM3 (TH) =',F10.5,/
386 $5X,'2. BULK DENSITY, G/CM3 (ROU) =',F10.5,/
387 $5X,'3. COLUMN LENGTH, CM (COL) =',F10.5,/
388 $5X,'4. WATER FLUX, CM/HR (WFLX) =',F10.5,/
389 $5X,'5. INITIAL CONCENTRATION, MG/L (CI) =',F10.5,/
390 $5X,'6. CONCEN. IN INPUT PULSE, MG/L (CJ) =',F10.5,/
391 $5X,'7. DISPERSION COEFFICIENT, CM2/HR (D) =',F10.5,/
392 $5X,'8. FORWARD RATE REACTION, K1,HR-1 (K1) =',F10.5,/
393 $5X,'9. BACKWARD RATE REACTION, K2,HR-1 (K2) =',F10.5,/
394 $4X,'10. FORWARD RATE REACTION, K3,HR-1 (K3) =',F10.5,/
395 $4X,'11. BACKWARD RATE REACTION, K4,HR-1 (K4) =',F10.5,/
396 $4X,'12. FRACTION, F (F) =',F10.5,/
397 $4X,'13. TOTAL SORPTION SITES (ST) =',F10.5,/
398 $4X,'14. IRREVERSIBLE REACTION RATE,KS,HR-1 (KS) =',F10.5)
399 310 FORMAT(
400 $4X,'15. NUMBER OF ITERATIONS (IT) =',I10,/
401 $4X,'16. INPUT PULSE DURATION, HR (TPULSE) =',F10.5,/
402 $4X,'17. TOTAL SIMULATION TIME, HR (TTOTAL) =',F10.5,/
403 $4X,'18. PRINTOUT TIME DESIRED, HR (TPRINT) =',F10.5,////)
404 340 FORMAT(//,
405 $5X,'1. KAPPA1 (DIMENSIONLESS K1 ) =',F10.5,/
406 $5X,'2. KAPPA2 (DIMENSIONLESS K2 ) =',F10.5,/
407 $5X,'3. KAPPA1 (DIMENSIONLESS K3 ) =',F10.5,/
408 $5X,'4. KAPPA2 (DIMENSIONLESS K4 ) =',F10.5,/
409 $5X,'5. KAPPAS (DIMENSIONLESS KS ) =',F10.5,/
410 $5X,'6. OMEGA (DIMENSIONLESS ST ) =',F10.5,/
411 $5X,'7. PECLET NUMBER (WFLX*COL/D*TH) =',F10.5,////)
412 400 FORMAT(2X,'THE INCREMENTS USED WERE :',//
413 $5X,'1. SIMULATION DEPTH INTERVAL,CM (DX) =',F12.6,/
414 $5X,'2. INCREMENTAL TIME STEP,HR (DT) =',F12.6,////)

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415      500  FORMAT(////////,2X,
416      $'S I M U L A T I O N   T I M E   (HR)   =' ,F8.2)
417      525  FORMAT(2X,
418      $'PORE VOLUMES (V/V0) =' ,F10.2,8X,'REL. CONCENTRATION (C/C0) =' ,
419      &F8.4//)
420      550  FORMAT(
421      $1X,'DEPTH',04X,'CONCENTR.',T24,'VACANT '
422      $,T35,'VACANT',T45,'FILLED'
423      $,T56,'FILLED ',T67,'IRREV.')
424      560  FORMAT(
425      $T24,'SITES I',T34,'SITES II',T45,'SITES I',T56,'SITES II',
426      $T67,' SINK ')
427      570  FORMAT(
428      $2X,'(CM)',T12,'(PPM)',T26,'(MG)',T36,'(MG)',T46,'(MG)',T57,'(MG)',
429      $T68,'(MG)'//)
430      600  FORMAT(1X,F6.2,F12.4,1X,F12.4,1X,F09.3,1X,F09.3,1X,F09.3,F11.3)
431      650  FORMAT(////////,2X,'SIMULATIONS ARE NOW COMPLETE UP TO',///,5X,
432      $'S I M U L A T I O N   T I M E   (HRS)   =' ,F8.2,///2X,
433      $'PORE VOLUMES (V/V0) =' ,F10.2,8X,'REL. CONCENTRATION (C/C0) =' ,
434      &F8.4//)
435      700  FORMAT(50X,E10.6)
436      750  FORMAT(50X,I3)
437      800  FORMAT(A64)
438      900  FORMAT(F12.0)
439      950  FORMAT(I1)
440      WRITE(*,*)
441      WRITE(*,*) '----- Requested Simulations Completed -----'
442      WRITE(*,*)
443      WRITE(*,*) '----- SOTSPC Program Terminated Successfully -----'
444      WRITE(*,*)
445      WRITE(*,*) '----- THANK YOU FOR USING SOTSPC -----'
446      END
447
448      C
449      C
450      C      *****
451      SUBROUTINE TRIDM(A,B,C,D,N)
452      IMPLICIT REAL*8 (A-H,O-Z)
453      DIMENSION A(N),B(N),C(N),D(N)
454      DO 1 I=2,N
455      C(I)=C(I)/A(I-1)
456      A(I)=A(I)-(C(I)*B(I-1))
457      1 CONTINUE
458      DO 2 I=2,N
459      D(I)=D(I)-(C(I)*D(I-1))
460      2 CONTINUE
461      D(N)=D(N)/A(N)
462      DO 3 I=2,N
463      D(N+1-I)=(D(N+1-I)-(B(N+1-I)*D(N+2-I)))/A(N+1-I)
464      3 CONTINUE
465      RETURN
466      END
467
468      C
469      C      *****
470      SUBROUTINE INTEG PERFORMS INTEGRATION OF A TABULAR FUNCTION Y
471      C      GIVEN AT EQUAL DISTANCES H USING TRAPEZOIDAL RULE.
472      C      *****
473      C
474      SUBROUTINE INTEG(H,Y,Z,N)
475      IMPLICIT REAL*8 (A-H,O-Z)
476      DIMENSION Y(N),Z(N)
477      S2=0.0D0
478      IF(N-1) 40,30,10
479      10 HH=H/2.0D0
480      DO 20 I =2,N
481      S1=S2
482      S2=S2+HH*(Y(I)+Y(I-1))
483      20 Z(I-1)=S1
484      30 Z(N)=S2
485      40 RETURN
486      END

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Sample of SOTS Model Input Data

1. MOISTURE CONTENT, CM3/CM3	(TH) = 0.400E00
2. BULK DENSITY, G/CM3	(ROU) = 1.200E00
3. COLUMN LENGTH, CM	(COL) = 10.000E00
4. WATER FLUX, CM/HR	(WFLX) = 1.000E00
5. INITIAL CONCENTRATION, PPM	(CI) = 0.000E00
6. CONCEN. IN INPUT PULSE, PPM	(CS) = 100.000E00
7. DISPERSION COEFFICIENT., CM2/HR	(D) = 1.000E00
8. TOTAL AMOUNT OF AVAILABLE SITES, ST	(ST) = 166.660E00
9. FRACTION OF TYPE I SITES, F	(F) = 0.500E00
10. FORWARD RATE REACTION, K1, HR-1	(K1) = 0.007500
11. BACKWARD RATE REACTION, K2, HR-1	(K2) = 0.250E-0
12. FORWARD RATE REACTION, K3, HR-1	(K3) = 0.000750
13. BACKWARD RATE REACTION, K4, HR-1	(K4) = 0.025E-0
14. IRREVERSIBLE REACTION RATE, KS, HR-1	(KS) = 0.000E-0
15. NUMBER OF ITERATIONS	(IT) 000
16. INPUT PULSE DURATION, HR	(TPULSE) = 12.000E00
17. TOTAL SIMULATION TIME, HR	(TTOTAL) = 16.000E00
18. PRINTOUT TIME DESIRED, HR	(TPRINT) = 4.000E00
19. INCREMENTAL TIME STEP, HR	(DT) = 0.100E00
20. INCREMENTAL DISTANCE, CM	(DX) = 1.000E00

SOTS Model Computer Program Output Listing

WELCOME TO

P C V E R S I O N O F

SECOND - ORDER TWO - SITE MODEL

S. O. T. S.

SIMULATION MODEL FOR TRANSPORT

AND RETENTION OF HEAVY METALS IN SOILS

UNDER STEADY - STATE WATER CONDITIONS

PROGRAM WRITTEN AND DOCUMENTED

by
H. M. SELIM
February 1990

INPUT PARAMETERS :

1.	MOISTURE CONTENT, CM3/CM3	(TH)	=	.40000
2.	BULK DENSITY, G/CM3	(ROU)	=	1.20000
3.	COLUMN LENGTH, CM	(COL)	=	10.00000
4.	WATER FLUX, CM/HR	(WFLX)	=	1.00000
5.	INITIAL CONCENTRATION, MG/L	(CI)	=	.00000
6.	CONCEN. IN INPUT PULSE, MG/L	(CS)	=	100.00000
7.	DISPERSION COEFFICIENT, CM2/HR	(D)	=	1.00000
8.	FORWARD RATE REACTION, K1,HR-1	(K1)	=	.00750
9.	BACKWARD RATE REACTION, K2,HR-1	(K2)	=	.25000
10.	FORWARD RATE REACTION, K3,HR-1	(K3)	=	.00075
11.	BACKWARD RATE REACTION, K4,HR-1	(K4)	=	.02500
12.	FRACTION, F	(F)	=	.50000
13.	TOTAL SORPTION SITES	(ST)	=	166.66000
14.	IRREVERSIBLE REACTION RATE, KS,HR-1	(KS)	=	.00000
15.	NUMBER OF ITERATIONS	(IT)	=	0
16.	INPUT PULSE DURATION, HR	(TPULSE)	=	12.00000
17.	TOTAL SIMULATION TIME, HR	(TTOTAL)	=	16.00000
18.	PRINTOUT TIME DESIRED, HR	(TPRINT)	=	4.00000

THE INCREMENTS USED WERE :

1.	SIMULATION DEPTH INTERVAL,CM	(DX)	=	.250000
2.	INCREMENTAL TIME STEP,HR	(DT)	=	.020000
1.	KAPPA1	(DIMENSIONLESS K1)	=	1.00000
2.	KAPPA2	(DIMENSIONLESS K2)	=	1.00000
3.	KAPPA1	(DIMENSIONLESS K3)	=	.10000
4.	KAPPA2	(DIMENSIONLESS K4)	=	.10000
5.	KAPPAS	(DIMENSIONLESS KS)	=	.00000
6.	OMEGA	(DIMENSIONLESS ST)	=	.00000
7.	PECLET NUMBER	(WFLX*COL/D*TH)	=	25.00000

S I M U L A T I O N T I M E (HR) = 4.00
 PORE VOLUMES (V/V0) = 1.00 REL. CONCENTRATION (C/C0) = .0906

DEPTH (CM)	CONCENTR. (PPM)	VACANT SITES I (MG)	VACANT SITES II (MG)	FILLED SITES I (MG)	FILLED SITES II (MG)	IRREV. SINK (MG)
.00	97.0155	48.8210	76.375	34.509	6.955	.000
.25	95.2415	49.8403	76.750	33.490	6.580	.000
.50	93.3256	50.9025	77.117	32.427	6.213	.000
.75	91.2793	52.0045	77.474	31.326	5.856	.000
1.00	89.1067	53.1421	77.822	30.188	5.508	.000
1.25	86.8134	54.3110	78.160	29.019	5.170	.000
1.50	84.4064	55.5063	78.487	27.824	4.843	.000
1.75	81.8942	56.7228	78.803	26.607	4.527	.000
2.00	79.2865	57.9549	79.107	25.375	4.223	.000
2.25	76.5942	59.1968	79.399	24.133	3.931	.000
2.50	73.8291	60.4426	79.679	22.887	3.651	.000
2.75	71.0038	61.6865	79.947	21.644	3.383	.000
3.00	68.1313	62.9224	80.202	20.408	3.128	.000
3.25	65.2252	64.1448	80.445	19.185	2.885	.000
3.50	62.2989	65.3480	80.675	17.982	2.655	.000
3.75	59.3657	66.5270	80.892	16.803	2.438	.000
4.00	56.4388	67.6769	81.097	15.653	2.233	.000
4.25	53.5308	68.7934	81.290	14.537	2.040	.000
4.50	50.6533	69.8726	81.471	13.457	1.859	.000
4.75	47.8175	70.9112	81.639	12.419	1.691	.000
5.00	45.0335	71.9063	81.797	11.424	1.533	.000
5.25	42.3105	72.8558	81.943	10.474	1.387	.000
5.50	39.6564	73.7577	82.079	9.572	1.251	.000
5.75	37.0784	74.6110	82.205	8.719	1.125	.000
6.00	34.5825	75.4150	82.320	7.915	1.010	.000
6.25	32.1736	76.1693	82.427	7.161	.903	.000
6.50	29.8557	76.8742	82.524	6.456	.806	.000
6.75	27.6320	77.5301	82.614	5.800	.716	.000
7.00	25.5048	78.1382	82.695	5.192	.635	.000
7.25	23.4758	78.6994	82.769	4.631	.561	.000
7.50	21.5458	79.2155	82.835	4.115	.495	.000
7.75	19.7152	79.6879	82.896	3.642	.434	.000
8.00	17.9840	80.1187	82.950	3.211	.380	.000
8.25	16.3518	80.5098	82.999	2.820	.331	.000
8.50	14.8183	80.8633	83.042	2.467	.288	.000
8.75	13.3841	81.1810	83.081	2.149	.249	.000
9.00	12.0534	81.4645	83.115	1.865	.215	.000
9.25	10.8412	81.7133	83.145	1.617	.185	.000
9.50	9.7955	81.9213	83.170	1.409	.160	.000
9.75	9.0605	82.0644	83.187	1.266	.143	.000
10.00	9.0605	82.0644	83.187	1.266	.143	.000

S A L T B A L A N C E :

TOTAL INPUT SALT FROM PULSE	(MG)	=	400.0000
TOTAL SALT IN SOIL SOLUTION PHASE	(MG)	=	192.2133
TOTAL SORBED IN TYPE I SITES S1	(MG)	=	166.5461
TOTAL SORBED IN TYPE II SITES S2	(MG)	=	26.7511
TOTAL SORBED IN IRREVERSIBLE PHASE	(MG)	=	.0000
TOTAL SALT IN THE EFFLUENT	(MG)	=	7.0755
MASS BALANCE (CALC.OUTPUT/INPUT)	(%)	=	98.1465

S I M U L A T I O N T I M E (HR) = 8.00
 PORE VOLUMES (V/V0) = 2.00 REL. CONCENTRATION (C/C0) = .3679

DEPTH (CM)	CONCENTR. (PPM)	VACANT SITES I (MG)	VACANT SITES II (MG)	FILLED SITES I (MG)	FILLED SITES II (MG)	IRREV. SINK (MG)
.00	98.8940	42.9216	70.199	40.408	13.131	.000
.25	98.2309	43.2425	70.579	40.088	12.751	.000
.50	97.5205	43.5881	70.957	39.742	12.373	.000
.75	96.7620	43.9594	71.335	39.371	11.995	.000
1.00	95.9525	44.3575	71.712	38.973	11.618	.000
1.25	95.0892	44.7832	72.087	38.547	11.243	.000
1.50	94.1695	45.2374	72.460	38.093	10.870	.000
1.75	93.1907	45.7207	72.831	37.609	10.499	.000
2.00	92.1507	46.2339	73.200	37.096	10.130	.000
2.25	91.0474	46.7772	73.565	36.553	9.765	.000
2.50	89.8790	47.3511	73.927	35.979	9.403	.000
2.75	88.6441	47.9555	74.286	35.375	9.044	.000
3.00	87.3417	48.5903	74.640	34.740	8.690	.000
3.25	85.9711	49.2553	74.990	34.075	8.340	.000
3.50	84.5323	49.9499	75.335	33.380	7.995	.000
3.75	83.0256	50.6734	75.674	32.657	7.656	.000
4.00	81.4518	51.4246	76.008	31.905	7.322	.000
4.25	79.8124	52.2025	76.335	31.127	6.995	.000
4.50	78.1094	53.0055	76.656	30.325	6.674	.000
4.75	76.3452	53.8319	76.970	29.498	6.360	.000
5.00	74.5231	54.6797	77.277	28.650	6.053	.000
5.25	72.6466	55.5468	77.577	27.783	5.753	.000
5.50	70.7198	56.4310	77.868	26.899	5.462	.000
5.75	68.7474	57.3295	78.152	26.000	5.178	.000
6.00	66.7345	58.2399	78.427	25.090	4.903	.000
6.25	64.6864	59.1593	78.693	24.171	4.637	.000
6.50	62.6090	60.0849	78.951	23.245	4.379	.000
6.75	60.5082	61.0136	79.200	22.316	4.130	.000
7.00	58.3903	61.9427	79.440	21.387	3.890	.000
7.25	56.2616	62.8691	79.671	20.461	3.659	.000
7.50	54.1285	63.7899	79.892	19.540	3.438	.000
7.75	51.9975	64.7023	80.105	18.628	3.225	.000
8.00	49.8750	65.6035	80.308	17.727	3.022	.000
8.25	47.7678	66.4906	80.502	16.839	2.828	.000
8.50	45.6834	67.3608	80.687	15.969	2.643	.000
8.75	43.6324	68.2101	80.863	15.120	2.467	.000
9.00	41.6332	69.0317	81.029	14.298	2.301	.000
9.25	39.7272	69.8103	81.182	13.520	2.148	.000
9.50	38.0191	70.5055	81.316	12.824	2.014	.000
9.75	36.7876	71.0067	81.411	12.323	1.919	.000
10.00	36.7876	71.0067	81.411	12.323	1.919	.000

S A L T B A L A N C E :

TOTAL INPUT SALT FROM PULSE (MG) = 800.0000
 TOTAL SALT IN SOIL SOLUTION PHASE (MG) = 286.2145
 TOTAL SORBED IN TYPE I SITES S1 (MG) = 331.2864
 TOTAL SORBED IN TYPE II SITES S2 (MG) = 78.3887
 TOTAL SORBED IN IRREVERSIBLE PHASE (MG) = .0000
 TOTAL SALT IN THE EFFLUENT (MG) = 97.8128
 MASS BALANCE (CALC.OUTPUT/INPUT) () = 99.2128

S I M U L A T I O N T I M E (HR) = 12.00
 PORE VOLUMES (V/V0) = 3.00 REL. CONCENTRATION (C/C0) = .6246

DEPTH (CM)	CONCENTR. (PPM)	VACANT SITES I (MG)	VACANT SITES II (MG)	FILLED SITES I (MG)	FILLED SITES II (MG)	IRREV. SINK (MG)
.00	99.3425	41.9740	65.075	41.356	18.255	.000
.25	98.9407	42.1036	65.417	41.226	17.913	.000
.50	98.5233	42.2415	65.760	41.088	17.570	.000
.75	98.0899	42.3883	66.105	40.942	17.225	.000
1.00	97.6394	42.5445	66.451	40.785	16.879	.000
1.25	97.1705	42.7109	66.798	40.619	16.532	.000
1.50	96.6820	42.8881	67.147	40.442	16.183	.000
1.75	96.1726	43.0768	67.496	40.253	15.834	.000
2.00	95.6409	43.2776	67.846	40.052	15.484	.000
2.25	95.0854	43.4914	68.196	39.839	15.134	.000
2.50	94.5046	43.7188	68.547	39.611	14.783	.000
2.75	93.8972	43.9606	68.899	39.369	14.431	.000
3.00	93.2614	44.2176	69.250	39.112	14.080	.000
3.25	92.5958	44.4903	69.601	38.840	13.729	.000
3.50	91.8988	44.7797	69.953	38.550	13.377	.000
3.75	91.1687	45.0863	70.303	38.244	13.027	.000
4.00	90.4041	45.4110	70.653	37.919	12.677	.000
4.25	89.6034	45.7542	71.002	37.576	12.328	.000
4.50	88.7652	46.1167	71.350	37.213	11.980	.000
4.75	87.8880	46.4991	71.697	36.831	11.633	.000
5.00	86.9706	46.9017	72.042	36.428	11.288	.000
5.25	86.0117	47.3252	72.385	36.005	10.945	.000
5.50	85.0102	47.7699	72.725	35.560	10.605	.000
5.75	83.9652	48.2361	73.064	35.094	10.266	.000
6.00	82.8759	48.7239	73.399	34.606	9.931	.000
6.25	81.7418	49.2335	73.732	34.096	9.598	.000
6.50	80.5625	49.7650	74.061	33.565	9.269	.000
6.75	79.3379	50.3181	74.387	33.012	8.943	.000
7.00	78.0680	50.8927	74.708	32.437	8.622	.000
7.25	76.7533	51.4883	75.026	31.842	8.304	.000
7.50	75.3945	52.1045	75.339	31.225	7.991	.000
7.75	73.9926	52.7406	75.647	30.589	7.683	.000
8.00	72.5490	53.3957	75.950	29.934	7.380	.000
8.25	71.0661	54.0687	76.247	29.261	7.083	.000
8.50	69.5475	54.7578	76.539	28.572	6.791	.000
8.75	68.0006	55.4598	76.824	27.870	6.506	.000
9.00	66.4412	56.1679	77.100	27.162	6.230	.000
9.25	64.9079	56.8658	77.362	26.464	5.968	.000
9.50	63.4983	57.5102	77.596	25.820	5.734	.000
9.75	62.4646	57.9857	77.765	25.344	5.565	.000
10.00	62.4646	57.9857	77.765	25.344	5.565	.000

S A L T B A L A N C E :

TOTAL INPUT SALT FROM PULSE (MG) = 1200.0000
 TOTAL SALT IN SOIL SOLUTION PHASE (MG) = 337.7995
 TOTAL SORBED IN TYPE I SITES S1 (MG) = 422.0256
 TOTAL SORBED IN TYPE II SITES S2 (MG) = 137.2232
 TOTAL SORBED IN IRREVERSIBLE PHASE (MG) = .0000
 TOTAL SALT IN THE EFFLUENT (MG) = 299.4983
 MASS BALANCE (CALC.OUTPUT/INPUT) (%) = 99.7122

S I M U L A T I O N T I M E (HR) = 16.00
 PORE VOLUMES (V/V0) = 4.00 REL. CONCENTRATION (C/C0) = .5845

DEPTH (CM)	CONCENTR. (PPM)	VACANT SITES I (MG)	VACANT SITES II (MG)	FILLED SITES I (MG)	FILLED SITES II (MG)	IRREV. SINK (MG)
.00	2.2278	66.3619	66.380	16.968	16.950	.000
.25	3.5953	65.3925	66.438	17.938	16.892	.000
.50	4.9921	64.4567	66.504	18.873	16.826	.000
.75	6.4113	63.5539	66.578	19.776	16.752	.000
1.00	7.8512	62.6834	66.660	20.647	16.670	.000
1.25	9.3098	61.8445	66.749	21.485	16.581	.000
1.50	10.7853	61.0368	66.846	22.293	16.484	.000
1.75	12.2761	60.2596	66.951	23.070	16.379	.000
2.00	13.7806	59.5126	67.063	23.817	16.267	.000
2.25	15.2972	58.7955	67.183	24.535	16.147	.000
2.50	16.8245	58.1078	67.310	25.222	16.020	.000
2.75	18.3611	57.4493	67.444	25.881	15.886	.000
3.00	19.9058	56.8199	67.586	26.510	15.744	.000
3.25	21.4575	56.2194	67.734	27.111	15.596	.000
3.50	23.0151	55.6479	67.890	27.682	15.440	.000
3.75	24.5776	55.1052	68.052	28.225	15.278	.000
4.00	26.1442	54.5914	68.221	28.739	15.109	.000
4.25	27.7141	54.1068	68.397	29.223	14.933	.000
4.50	29.2868	53.6515	68.579	29.679	14.751	.000
4.75	30.8615	53.2257	68.767	30.104	14.563	.000
5.00	32.4375	52.8298	68.962	30.500	14.368	.000
5.25	34.0143	52.4642	69.163	30.866	14.167	.000
5.50	35.5909	52.1293	69.370	31.201	13.960	.000
5.75	37.1661	51.8256	69.583	31.504	13.747	.000
6.00	38.7385	51.5537	69.801	31.776	13.529	.000
6.25	40.3060	51.3141	70.025	32.016	13.305	.000
6.50	41.8662	51.1074	70.255	32.223	13.075	.000
6.75	43.4157	50.9342	70.490	32.396	12.840	.000
7.00	44.9502	50.7951	70.729	32.535	12.601	.000
7.25	46.4648	50.6907	70.974	32.639	12.356	.000
7.50	47.9534	50.6214	71.223	32.709	12.107	.000
7.75	49.4088	50.5879	71.476	32.742	11.854	.000
8.00	50.8232	50.5904	71.734	32.740	11.596	.000
8.25	52.1875	50.6290	71.995	32.701	11.335	.000
8.50	53.4920	50.7037	72.259	32.626	11.071	.000
8.75	54.7261	50.8134	72.525	32.517	10.805	.000
9.00	55.8764	50.9553	72.790	32.375	10.540	.000
9.25	56.9223	51.1223	73.048	32.208	10.282	.000
9.50	57.8190	51.2964	73.284	32.034	10.046	.000
9.75	58.4450	51.4343	73.457	31.896	9.873	.000
10.00	58.4450	51.4343	73.457	31.896	9.873	.000

S A L T B A L A N C E :

TOTAL INPUT SALT FROM PULSE (MG) = 1200.0000
 TOTAL SALT IN SOIL SOLUTION PHASE (MG) = 128.5387
 TOTAL SORBED IN TYPE I SITES S1 (MG) = 341.2330
 TOTAL SORBED IN TYPE II SITES S2 (MG) = 167.7559
 TOTAL SORBED IN IRREVERSIBLE PHASE (MG) = .0000
 TOTAL SALT IN THE EFFLUENT (MG) = 568.6738
 MASS BALANCE (CALC.OUTPUT/INPUT) (%) = 100.5168

APPENDIX D: SOMIM

Computer Program Listing

```

1      C
2      $LARGE
3      C*****
4      C
5      C          ***** S. O. M. I. M. *****
6      C
7      C          SECOND - ORDER    MOBILE - IMMOBILE    MODEL
8      C
9      C*****
10     C
11     C          COMPUTER PROGRAM
12     C
13     C    FOR THE TRANSPORT AND RETENTION OF HEAVY METALS IN SOILS
14     C
15     C          UNDER STEADY - STATE WATER FLUX CONDITIONS
16     C
17     C          USING
18     C
19     C          THE CONVECTIVE - DISPERSIVE EQUATION
20     C
21     C          WITH THE MOBILE - IMMOBILE WATER CONCEPT
22     C
23     C          WITH
24     C
25     C    REVERSIBLE SECOND - ORDER KINETICS AND IRREVERSIBLE REACTIONS
26     C
27     C*****
28     C
29     C          PROGRAM WRITTEN AND DOCUMENTED
30     C
31     C          by
32     C
33     C          H. M. SELIM
34     C          February 1990
35     C*****
36     C
37     C    IMPLICIT REAL*8 (A-H,O-Z)
38     C    CHARACTER*64 FNAMEI,FNAMEO
39     C    DIMENSION DC(501),DU(501),DL(501),E(501),CM(501),CIM(501)
40     C    DIMENSION CMX(501),CIMN(501)
41     C    DIMENSION SIR(501),SM(501),SMX(501),SIM(501)
42     C    CHARACTER*64 USER,SOIL,SOLUTE,DATE
43     C    REAL*8 K1,K2,KS,KAPPA1,KAPPA2,KAPPAS
44     C
45     C
46     C    WRITE(*,100)
47     C --- READ INPUT PARAMETERS -----
48     C
49     C    WRITE(*,*) ' PLEASE ENTER USER NAME (OPTIONAL):'
50     C    READ(*,800) USER
51     C    WRITE(*,*) ' PLEASE ENTER NAME OF SOIL (OPTIONAL):'
52     C    READ(*,800) SOIL
53     C    WRITE(*,*) ' PLEASE ENTER NAME OF SOLUTE (OPTIONAL):'
54     C    READ(*,800) SOLUTE
55     C    WRITE(*,*) ' ENTER DATE OR OTHER IDENTIFICATION (OPTIONAL):'
56     C    READ(*,800) 53 DATE
57     C    WRITE(*,*) ' '
58     C    WRITE(*,*)
59     C    $' ----- INPUT PARAMETERS SECTION -----'
60     C    WRITE(*,*) ' '
61     C    WRITE(*,*) ' INPUT PARAMETERS CAN BE PROVIDED IN TWO WAYS;'
62     C    WRITE(*,*) ' ENTER 1 if you wish to enter the input data using'
63     C    WRITE(*,*) ' the keyboard (i.e. interactively);'
64     C    WRITE(*,*) ' '

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65         WRITE(*,*) '                                OR'
66         WRITE(*,*) ' '
67         WRITE(*,*) '     ENTER 2 if an input data file is to be provided'
68         WRITE(*,*)
69         $'          PLEASE ENTER EITHER 1 OR 2'
70         READ(*,950) IFLAG
71         IF(IFLAG.NE.1) THEN
72             WRITE(*, '(A)') '     PLEASE ENTER NAME OF INPUT FILE?'
73             WRITE(*,*) '(for example A:XX.DAT or C:UU.DAT for hard disk)'
74             READ(*, '(A)') FNAMEI
75             OPEN(5, FILE=FNAMEI)
76     C
77         READ(5,700) TH,ROU,COL,WFLX
78         READ(5,700) CI,CS,D,ST,F,FTH
79         READ(5,700) K1,K2,KS,TR
80         READ(5,750) IT
81         READ(5,700) TPULSE,TTOTAL,TPRINT,DT,DZ
82     C
83         ELSE
84     C
85         WRITE(*,*)
86         $'PLEASE ENTER THE FOLLOWING INPUT PARAMETERS : '
87         WRITE(*,*) ' '
88         WRITE(*,*)
89         $' (1) MOISTURE CONTENT,CM3/CM3                (TH)   ='
90         WRITE(*,*)
91         $' (Values usually less than 0.65 cm3/cm3). Enter your value NOW'
92         READ(*,900) TH
93         WRITE(*,*)
94         $' (2) BULK DENSITY,G/CM3                      (ROU)   ='
95         WRITE(*,*)
96         $' (Range of values 1.1 - 1.7 g/cm3). Enter your value NOW'
97         READ(*,900) ROU
98         WRITE(*,*)
99         $' (3) COLUMN LENGTH (CM)                      (COL)   ='
100        READ(*,900) COL
101        WRITE(*,*)
102        $' (4) WATER FLUX      (CM/HR)                  (WFLX)  ='
103        WRITE(*,*)
104        $' (Range of values 0.01 - 5 cm/hr). Enter your value NOW'
105        READ(*,900) WFLX
106        WRITE(*,*)
107        $' (5) INITIAL CONCENTRATION,                  (CI)    ='
108        READ(*,900) CI
109        WRITE(*,*)
110        $' (6) APPLIED CONCENTRATION,                  (CS)    ='
111        READ(*,900) CS
112        WRITE(*,*)
113        $' (7) DISPERSION COEFFICIENT, (CM2/HR)        (D)     ='
114        WRITE(*,*)
115        $' (Range of values 0.1 - 1.5 cm2/hour). Enter your value NOW'
116        READ(*,900) D
117        WRITE(*,*)
118        $' (8) TOTAL SORPTION SITES                    (ST)    ='
119        READ(*,900) ST
120        WRITE(*,*) '(Ranges from 200 to 2000 mg/kg). Enter your value NOW'
121        WRITE(*,*)
122        $' (9) FRACTION OF SITES, F                    (F)     ='
123        WRITE(*,*) '(Ranges from 0.0 to 1.0). Enter your value NOW'
124        READ(*,900) F
125        WRITE(*,*)
126        $' (10) FRACTION OF MOBILE WATER, FTH          (FTH)   ='
127        WRITE(*,*) '(Ranges from 0.1 to 1.0). Enter your value NOW'
128        READ(*,900) FTH
129        WRITE(*,*)
130        $' (11) FORWARD RATE REACTION, K1,HR-1        (K1)    ='
131        WRITE(*,*) '(Ranges from 0.001-0.1 hr-1). Enter your value NOW'
132        READ(*,900) K1
133        WRITE(*,*)
134        $' (12) BACKWARD RATE REACTION, K2,HR-1        (K2)    ='

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135      WRITE(*,*) '(Ranges from 0.01 - 0.5 hr-1). Enter your value NOW'
136      READ(*,900)  KS
137      WRITE(*,*)
138      $' (13) IRREVERSIBLE REACTION RATE,KS,HR-1 (KS)   ='
139      WRITE(*,*)
140      WRITE(*,*) '(Range is 0.0001 - 0.5 hr-1). Enter your value NOW'
141      READ(*,900)  KS
142      WRITE(*,*)
143      $' (14) MASS TRANSFER COEFFICIENT,TR, HR-1 (TR)   ='
144      WRITE(*,*) '(Range is 0.01 - 0.1 hr-1). Enter your value NOW'
145      READ(*,900)  TR
146      WRITE(*,*)
147      $' (15) NUMBER OF ITERATIONS (IT) (Integer value from 0 to 9)'
148      READ(*,950)  IT
149      WRITE(*,*)
150      $' (16) INPUT PULSE DURATION,HR          (TPULSE)  ='
151      READ(*,900)  TPULSE
152      WRITE(*,*)
153      $' (17) TOTAL SIMULATION TIME,HR          (TTOTAL)  ='
154      READ(*,900)  TTOTAL
155      WRITE(*,*)
156      $' (18) PRINTOUT TIME DESIRED,HR          (TPRINT)  ='
157      READ(*,900)  TPRINT
158      WRITE(*,*)
159      $' (19) INCREMENTAL DISTANCE, CM          (DZ)      ='
160      WRITE(*,*)
161      $'      A default value of DZ=1.00 is given
162      READ(*,900)  DDZ
163      WRITE(*,*)
164      $' (20) INCREMENTAL TIME STEP,HR          (DT)      ='
165      WRITE(*,*)
166      $'      A default value of Dt=0.00 is given
167      READ(*,900)  DDT
168      ENDIF
169      C
170      ZIN=1.00
171      IF(DDZ.NE.0.0) THEN
172      DZ=DDZ
173      ELSE
174      DZ=ZIN
175      ENDIF
176      PIN=0.00
177      IF(DDT.NE.0.0) THEN
178      DT=DDT
179      ELSE
180      DT=PIN
181      ENDIF
182      C
183      WRITE(*,'(A)') '      PLEASE ENTER NAME OF OUTPUT FILE (FOR EXAMPLE
184      * B:ZC.DAT)'
185      READ(*,'(A)') FNAMEO
186      OPEN(6,FILE=FNAMEO,STATUS='UNKNOWN')
187      C
188      WRITE(6,100)
189      WRITE(6,800) USER
190      WRITE(6,800) SOIL
191      WRITE(6,800) SOLUTE
192      WRITE(6,800) DATE
193      WRITE(6,300) TH,POU,COL,WFLX,CI,CS,D,ST,F,FTH,K1,K2,KS,TR
194      WRITE(6,310) IT,TPULSE,TTOTAL,TPRINT
195      C
196      C
197      CO=CS
198      THM=TH*FTH
199      THIM=TH-THM
200      PV=WFLX/THM
201      C
202      KAPPA1=K1*TH*TH*COL*CS/(POU*WFLX)
203      KAPPA2=K2*TH*COL/WFLX
204      KAPPA3=K3*TH*COL/WFLX

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205      OMEGA=ST*ROU/(CS*TH)
206      PE=WFLX*COL/(TH*D)
207      TRANSC=TR*COL*TH/(WFLX*THIM)
208      WRITE(6,340) KAPPA1,KAPPA2,KAPPAS,OMEGA,TRANSC,PE
209  C
210      EF=0.0D0
211      TIME=0.0D0
212  C
213      5  CONTINUE
214      GAMMA=DT/(2.D0*DZ*DZ)
215      BETA=DT/DZ
216      IF((BETA*PV).GT.0.50D0) GO TO 7
217      IF((GAMMA*D/(BETA*PV)).LT.0.50D0) GO TO 6
218      GO TO 8
219      6  DZ=DZ/2
220      GO TO 5
221      7  DT=DT/2
222      GO TO 5
223      8  CONTINUE
224      N=COL/DZ+0.50D0
225      NM1=N-1
226      NM2=N-2
227      NP1=N+1
228      GAMMA=DT/(2*DZ*DZ)
229      BETA=DT/DZ
230      WRITE(*,400) DZ,DT
231      WRITE(6,400) DZ,DT
232      IF(N.LT.500) GO TO 9
233      WRITE(*,*) ' W A R N I N G '
234      WRITE(*,*)
235      &'Dimension of variables exceed 500. Did you increase array sizes'
236      WRITE(*,*)
237      &' If not, the program will terminate abruptly (see text).'
238      9  CONTINUE
239  C
240      DO 10 I=1,NP1
241      SIR(I)=0.0D0
242      SM(I)=0.0D0
243      SIM(I)=0.0D0
244      SMX(I)=0.0D0
245      CM(I)=CI
246      CMX(I)=CI
247      CIM(I)=CI
248      10  CIMN(I)=CI
249      WRITE(*,*) '----- Initial Conditions Completed -----'
250  C
251      WRITE(*,*) '----- Execution Begins -----'
252      WRITE(*,*) '----- Please Wait -----'
253  C
254      NKK=TPRINT/DT+0.50D0
255      KLM=TTOTAL/DT+0.50D0
256      KK=KLM/NKK+0.5D0
257  C
258      L=0
259      IT=IT+1
260      SINT=TPULSE*CS*WFLX
261      DO 90 JJ=1,KK
262      DO 70 LL=1,NKK
263      TT=LL*DT+(JJ-1)*TPRINT
264  C      IF(DABS(TT-TPULSE).LT.0.01D0) CS=0.0D0
265      L=L+1
266  C
267      CM(1)=(WFLX*2*DZ*CS+D*THM*CM(3))/(WFLX*2*DZ+D*THM)
268  C
269      DO 35 IJ=1,IT
270      M=2
271      DO 15 I=1,NM1
272      DC(I)=1.0D0+2.D0*GAMMA*D-BETA*PV
273      DU(I)=BETA*PV-GAMMA*D
274      E(I)=CM(M)+GAMMA*D*(CM(M+1)-2.0D0*CM(M)+CM(M-1))

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275      DL(I)=-GAMMA*D
276      M=I+2
277      15  CONTINUE
278      M=N
279      DC(NM1)=1.D0+GAMMA*D
280      E(1)=E(1)+GAMMA*D*CM(1)
281      C
282      DO 20 I=1,NM1
283      M=I+1
284      PHIM=F*ST-SM(M)
285      PHIMX=F*ST-SMX(M)
286      PHIIM=(1.0D0-F)*ST-SIM(M)
287      H1=((CM(M)+CMX(M))/2)*((PHIM+PHIMX)/2)
288      RKM=K1*THM*H1-K2*ROU*(SM(M)+SMX(M))/2
289      RKM=RKM+F*DT/THM
290      RKIM=K1*THIM*CIM(M)*PHIIM-ROU*K2*SIM(M)
291      RKIM=(1.0D0-F)*DT*RKIM/THM
292      E(I)=E(I)-RKM-RKIM
293      E(I)=E(I)-(CIMN(M)-CIM(M))*((THIM/THM)
294      C      E(I)=E(I)-DT*KS*((CM(M)+CMX(M))/2)-DT*KS*(THIM/THM)*CIM(M);
295      E(I)=E(I)-DT*KS*((CM(M)+CMX(M))/2)
296      20  CONTINUE
297      CALL TRIDM(DC,DU,DL,E,NM1)
298      DO 25 I=2,N
299      25  CMX(I)=E(I-1)
300      CMX(NP1)=CMX(N)
301      CMX(1)=CM(1)
302      DO 30 I=1,NP1
303      PHIM=F*ST-SM(I)
304      PHIMX=F*ST-SMX(I)
305      H1=((CM(I)+CMX(I))/2)*((PHIM+PHIMX)/2)
306      SMX(I)=SM(I)+DT*
307      &(K1*(THM/ROU)*H1-K2*(SM(I)+SMX(I))/2)
308      30  CONTINUE
309      35  CONTINUE
310      DO 40 I=1,NP1
311      40  CIM(I)=CIMN(I)
312      DO 45 I=1,N
313      PHIIM=(1.0D0-F)*ST-SIM(I)
314      RKIM=K1*THIM*CIM(I)*PHIIM-ROU*K2*SIM(I)
315      RKIM=(1.0D0-F)*DT*RKIM/THIM
316      CIMN(I)=CIM(I)-RKIM+
317      &DT*(TR/THIM)*(CMX(I)-CIM(I))
318      &-DT*KS*CIM(I)
319      H2=CIMN(I)*PHIIM
320      SIM(I)=SIM(I)+DT*
321      &(K1*(THIM/ROU)*H2-K2*SIM(I))
322      45  CONTINUE
323      SIM(NP1)=SIM(N)
324      CIMN(NP1)=CIMN(N)
325      DO 50 I=1,NP1
326      SIR(I)=SIR(I)+DT*KS/ROU*(THM*CM(I)+THIM*CIM(I))
327      CM(I)=CMX(I)
328      SM(I)=SMX(I)
329      50  CONTINUE
330      EF=CM(N)+EF
331      IF(TT.GT.TPULSE) CS=0.0D0
332      70  CONTINUE
333      TIME=JJ*TPRINT
334      C
335      WRITE(6,500) TIME
336      VV0=WFLX*TIME/(COL*TH)
337      CC0=CM(N)/C0
338      WRITE(6,525) VV0,CC0
339      WRITE(*,650) TIME,VV0,CC0
340      WRITE(*,*) '-----Execution Continues-----'
341      WRITE(*,*) '-----Please Wait-----'
342      C
343      WRITE(6,550)
344      WRITE(6,560)

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345      WRITE(6,570)
346      DO 20 I=1,NP1
347      Z=DE*(I-1)
348      STX=SM(I)+SIM(I)+SIR(I)
349      90  WRITE(6,600) Z,CM(I),CIM(I),SM(I),SIM(I),SIR(I),STX
350      CALL INTEG(DZ,CM,E,NP1)
351      TSMW=THM*E(NP1)
352      CALL INTEG(DZ,CIM,E,NP1)
353      TSIMW=THIM*E(NP1)
354      CALL INTEG(DZ,SM,E,NP1)
355      TSM=POU*F*E(NP1)
356      CALL INTEG(DZ,SIM,E,NP1)
357      TSIM=POU*(1.0D0-F)*E(NP1)
358      CALL INTEG(DZ,SIR,E,NP1)
359      TSIR=POU*E(NP1)
360      SINP=TIME*CS*WFLX
361      C
362      IF(SINP.GT.SINT) SINP=SINT
363      IF(CS.EQ.0.D0) SINP=SINT
364      TEFFL=EF*DT*WFLX
365      TSW=TSIMW+TSMW
366      BAL=(TEFFL+TSW+TSIR+TSM+TSIM)*100.0D0/SINP
367      WRITE(6,200) SINP,TSMW,TSIMW,TSM,TSIM,TSIR,TEFFL,BAL
368      90  CONTINUE
369      100  FORMAT(//,7X,
370      &'*****',
371      &'//,7X,
372      &'                                WELCOME TO                                ',
373      &'//,7X,
374      &'                                P C   V E R S I O N   O F                                ',
375      &'//,7X,
376      &'                                SECOND - ORDER MOBILE - IMMOBILE MODEL                                ',
377      &'//,7X,
378      &'                                S . O . M . I . M .                                ',
379      &'//,7X,
380      &'                                SIMULATION MODEL FOR TRANSPORT                                ',
381      &'//,7X,
382      &'                                AND RETENTION OF HEAVY METALS IN SOILS                                ',
383      &'//,7X,
384      &'                                UNDER STEADY - STATE WATER CONDITIONS                                ',
385      &'//,7X,
386      &'*****',
387      &'//,7X,
388      &'                                PROGRAM WRITTEN AND DOCUMENTED                                ',
389      &'//,7X,
390      &'                                by                                ',
391      &'//,7X,
392      &'                                H . M . SELIM                                ',
393      &'//,7X,
394      &'                                February 1980                                ',
395      &'//,7X,
396      &'*****',
397      &'//)
398      200  FORMAT(//,2X,'S A L T   B A L A N C E :',//
399      &7X,'TOTAL INPUT SALT FROM PULSE (MG)   ='//F10.4,/,
400      &7X,'TOTAL SALT IN MOBILE-WATER PHASE (MG) ='//F10.4,/,
401      &7X,'TOTAL SALT IN IMMOBILE-WATER PHASE (MG) ='//F10.4,/,
402      &7X,'TOTAL SORBED IN MOBILE PHASE SM (MG) ='//F10.4,/,
403      &7X,'TOTAL SORBED IN IMMOBILE PHASE SIM (MG) ='//F10.4,/,
404      &7X,'TOTAL SORBED IN IRREVERSIBLE PHASE (MG) ='//F10.4,/,
405      &7X,'TOTAL SALT IN THE EFFLUENT (MG)   ='//F10.4,/,
406      &7X,'MASS BALANCE (CALC.OUTPUT/INPUT) ( ) ='//F10.4,/)
407      300  FORMAT(//,
408      &5X,'INPUT PARAMETERS :',//
409      &5X,'1.  MOISTURE CONTENT, CM3/CM3 (TH)   ='//F10.5,/,
410      &5X,'2.  BULK DENSITY, G/CM3 (POU)   ='//F10.5,/,
411      &5X,'3.  COLUMN LENGTH, CM (COL)   ='//F10.5,/,
412      &5X,'4.  WATER FLUX, CM/HR (WFLX)   ='//F10.5,/,
413      &5X,'5.  INITIAL CONCENTRATION, MG/L (CI)   ='//F10.5,/,
414      &5X,'6.  CONCEN. IN INPUT PULSE, MG/L (CS)   ='//F10.5,/)

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415      $5X,'7.  DISPERSION COEFFICIENT, CM2/HR      (D)  =' ,F10.5,/
416      $5X,'8.  TOTAL SORPTION SITES                (ST)  =' ,F10.5,/
417      $5X,'9.  FRACTION OF SITES, F                (F)   =' ,F10.5,/
418      $4X,'10. FRACTION OF MOBILE WATER, FTH        (FTH)  =' ,F10.5,/
419      $4X,'11. FORWARD RATE REACTION, K1,HR-1      (K1)   =' ,F10.5,/
420      $4X,'12. BACKWARD RATE REACTION, K2,HR-1     (K2)   =' ,F10.5,/
421      $4X,'13. IRREVERSIBLE REACTION RATE,KS,HR-1 (KS)  =' ,F10.5,/
422      $4X,'14. MASS TRANSFER COEFFICIENT,TR, HR-1 (TR)  =' ,F10.5)
423      310  FORMAT(
424      $4X,'15.  NUMBER OF ITERATIONS                ==',I10,/
425      $4X,'16.  INPUT PULSE DURATION,HR             (TPULSE) =' ,F10.5,/
426      $4X,'17.  TOTAL SIMULATION TIME,HR           (TTOTAL) =' ,F10.5,/
427      $4X,'18.  PRINTOUT TIME DESIRED,HR           (TPRINT) =' ,F10.5,////)
428      340  FORMAT(//
429      $5X,'1.  KAPPA1      (DIMENSIONLESS K1 )      =' ,F10.5,/
430      $5X,'2.  KAPPA2      (DIMENSIONLESS K2 )      =' ,F10.5,/
431      $5X,'3.  KAPPAS      (DIMENSIONLESS KS )      =' ,F10.5,/
432      $5X,'4.  OMEGA        (DIMENSIONLESS ST )      =' ,F10.5,/
433      $5X,'5.  TRANSFER COEFFICIENT (DIMENSIONLESS ) =' ,F10.5,/
434      $5X,'6.  PECLET NUMBER (WFLX*COL/D*TH)        =' ,F10.5,////)
435      400  FORMAT(2X,'THE INCREMENTS USED WERE :',//
436      $5X,'1. SIMULATION DEPTH INTERVAL, CM      (DZ)  =' ,F12.6,/
437      $5X,'2. INCREMENTAL TIME STEP, HR          (DT)  =' ,F12.6,////)
438      500  FORMAT(////////,2X,
439      $'S I M U L A T I O N      T I M E (HR)  =' ,F8.2)
440      525  FORMAT(2X,
441      $'PORE VOLUMES (V/V0) =' ,F10.2,8X,'REL. CONCENTRATION (C/C0) =' ,
442      &F8.4/)
443      550  FORMAT(
444      $1X,'DEPTH',06X,'CONCENT.',T25,'CONCENT.'
445      $,T36,'SORBED',T47,'SORBED'
446      $,T56,'IRREVERS',T67,'TOTAL')
447      560  FORMAT(12X,'MOBILE',
448      $T25,'IMMOBILE',T36,'MOBILE',T46,'IMMOBILE',T58,'SINK',
449      $T67,'SORBED')
450      570  FORMAT(2X,'(CM)',T13,'(PPM)',T26,'(PPM)',T37,'(MG)',T48,'(MG)',
451      $T58,'(MG)',T68,'(MG)')
452      600  FORMAT(1X,F6.2,F12.4,1X,F12.4,1X,F09.3,1X,F09.3,1X,F09.3,F11.3)
453      650  FORMAT(////////,2X,'SIMULATIONS ARE NOW COMPLETE UP TO',///,5X,
454      $'S I M U L A T I O N      T I M E (HR)  =' ,F8.2,///2X,
455      $'PORE VOLUMES (V/V0) =' ,F10.2,8X,'REL. CONCENTRATION (C/C0) =' ,
456      &F8.4/)
457      700  FORMAT(50X,E10.6)
458      750  FORMAT(50X,I3)
459      800  FORMAT(A64)
460      900  FORMAT(F12.0)
461      950  FORMAT(I1)
462      WRITE(*,*)
463      WRITE(*,*) '----- Requested Simulations Completed -----'
464      WRITE(*,*)
465      WRITE(*,*) '----- SOMIMPC TERMINATED SUCCESSFULLY -----'
466      WRITE(*,*)
467      WRITE(*,*) '----- THANK YOU FOR USING MIMPC -----'
468      END
469      C
470      C
471      C *****
472      C
473      SUBROUTINE TRIDM(A,B,C,D,N)
474      IMPLICIT REAL*8(A-H,O-Z)
475      DIMENSION A(1),B(1),C(1),D(1)
476      DO 1 I=2,N
477      C(I)=C(I)/A(I-1)
478      A(I)=A(I)-(C(I)*B(I-1))
479      1 CONTINUE
480      DO 2 I=2,N
481      D(I)=D(I)-(C(I)*D(I-1))
482      2 CONTINUE
483      D(N)=D(N)/A(N)
484      DO 3 I=2,N

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485      D(N+1-I)=(D(N+1-I)-(B(N+1-I)*D(N+2-I)))/A(N+1-I)
486 3 CONTINUE
487 RETURN
488 END
489 C
490 SUBROUTINE INTEG(H,Y,Z,N)
491 IMPLICIT REAL*8(A-H,O-Z)
492 DIMENSION Y(N),Z(N)
493 S2=0.0D0
494 IF(N-1) 40,30,10
495 10 HH=H/2.0D0
496 DO 20 I =2,N
497 S1=S2
498 S2=S2+HH*(Y(I)+Y(I-1))
499 20 Z(I-1)=S1
500 30 Z(N)=S2
501 40 RETURN
502 END

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Sample of SOMIM Input Data

1.	MOISTURE CONTENT, CM3/CM3	(TH) =	0.400E00
2.	BULK DENSITY, G/CM3	(ROU) =	1.200E00
3.	COLUMN LENGTH, CM	(COL) =	10.000E00
4.	WATER FLUX, CM/HR	(WFLX) =	1.000E00
5.	INITIAL CONCENTRATION, MG/L	(CI) =	0.000E00
6.	CONCEN. IN INPUT PULSE, MG/L	(CS) =	100.000E00
7.	DISPERSION COEFFICIENT, CM2/HR	(D) =	1.000E00
8.	TOTAL ST	(ST) =	166.660E00
9.	FRACTION OF SITES, F	(F) =	0.500E00
10.	FRACTION OF WATER, FTH	(FTH) =	0.500E00
11.	FORWARD RATE REACTION, K1, HR-1	(K1) =	0.007500
12.	BACKWARD RATE REACTION, K2, HR-1	(K2) =	0.250E-0
13.	IRREVERSIBLE REACTION RATE, KS, HR-1	(KS) =	0.000E-0
14.	TRANSFER COEFFICIENT, TR	(TR) =	0.050E-0
15.	NUMBER OF ITERATIONS	(IT) =	000
16.	INPUT PULSE DURATION, HR	(TPULSE) =	12.00E00
17.	TOTAL SIMULATION TIME, HR	(TTOTAL) =	16.00E00
18.	PRINTOUT TIME DESIRED, HR	(TPRINT) =	4.00E00
19.	INCREMENTAL TIME STEP, HR	(DT) =	0.10E00
20.	INCREMENTAL DISTANCE, CM	(DZ) =	1.00E00

SOMIM Computer Program Output Listing

WELCOME TO
P C V E R S I O N O F
SECOND - ORDER MOBILE - IMMOBILE MODEL
S. O. M. I. M.
SIMULATION MODEL FOR TRANSPORT
AND RETENTION OF HEAVY METALS IN SOILS
UNDER STEADY - STATE WATER CONDITIONS

PROGRAM WRITTEN AND DOCUMENTED
by
H. M. SELIM
February 1990

INPUT PARAMETERS :

1.	MOISTURE CONTENT, CM3/CM3	(TH)	=	.40000
2.	BULK DENSITY, G/CM3	(ROU)	=	1.20000
3.	COLUMN LENGTH, CM	(COL)	=	10.00000
4.	WATER FLUX, M/HR	(WFLX)	=	1.00000
5.	INITIAL CONCENTRATION, MG/L	(CI)	=	.00000
6.	CONCEN. IN INPUT PULSE, MG/L	(CS)	=	100.00000
7.	DISPERSION COEFFICIENT.,CM2/HR	(D)	=	1.00000
8.	TOTAL SORPTION SITES	(ST)	=	166.66000
9.	FRACTION OF SITES, F	(F)	=	.50000
10.	FRACTION OF MOBILE WATER, FTH	(FTH)	=	.50000
11.	FORWARD RATE REACTION, K1,HR-1	(K1)	=	.00750
12.	BACKWARD RATE REACTION, K2,HR-1	(K2)	=	.25000
13.	IRREVERSIBLE REACTION RATE,KS,HR-1	(KS)	=	.00000
14.	MASS TRANSFER COEFFICIENT,TR, HR-1	(TR)	=	.05000
15.	NUMBER OF ITERATIONS		=	0
16.	INPUT PULSE DURATION,HR	(TPULSE)	=	12.00000
17.	TOTAL SIMULATION TIME,HR	(TTOTAL)	=	16.00000
18.	PRINTOUT TIME DESIRED,HR	(TPRINT)	=	4.00000
1.	KAPPA1	(DIMENSIONLESS K1)	=	1.00000
2.	KAPPA2	(DIMENSIONLESS K2)	=	1.00000
3.	KAPPAS	(DIMENSIONLESS KS)	=	.00000
4.	OMEGA	(DIMENSIONLESS ST)	=	4.99980
5.	TRANSFER COEFFICIENT (DIMENSIONLESS)		=	1.00000
6.	PECLET NUMBER (WFLX*COL/D*TH)		=	25.00000

THE INCREMENTS USED WERE :

1.	SIMULATION DEPTH INTERVAL, CM	(DZ)	=	.125000
2.	INCREMENTAL TIME STEP, HR	(DT)	=	.010000

S I M U L A T I O N T I M E (HR) = 4.01
 PORE VOLUMES (V/VG) = 1.00 REL. CONCENTRATION (C/C0) = .5014

DEPTH (CM)	CONCENT. MOBILE (PPM)	CONCENT. IMMOBILE (PPM)	SORBED MOBILE (MG)	SORBED IMMOBILE (MG)	IRFEVERS SINK (MG)	TOTAL SORBED (MG)
.00	99.1580	46.0052	21.281	7.872	.000	29.153
.13	98.6365	45.9283	21.087	7.758	.000	28.845
.25	98.1094	45.0222	20.894	7.633	.000	28.526
.38	97.5775	44.5179	20.699	7.508	.000	28.208
.50	97.0409	44.0154	20.505	7.385	.000	27.889
.63	96.4997	43.5147	20.309	7.263	.000	27.572
.75	95.9540	43.0159	20.113	7.141	.000	27.255
.88	95.4038	42.5190	19.917	7.021	.000	26.938
1.00	94.8492	42.0240	19.720	6.902	.000	26.622
1.13	94.2902	41.5309	19.523	6.784	.000	26.307
1.25	93.7270	41.0399	19.325	6.668	.000	25.993
1.38	93.1596	40.5510	19.127	6.552	.000	25.679
1.50	92.5881	40.0641	18.929	6.437	.000	25.366
1.63	92.0126	39.5793	18.731	6.324	.000	25.054
1.75	91.4331	39.0967	18.532	6.211	.000	24.743
1.88	90.8497	38.6163	18.333	6.100	.000	24.433
2.00	90.2626	38.1381	18.134	5.990	.000	24.124
2.13	89.6718	37.6622	17.935	5.881	.000	23.816
2.25	89.0773	37.1885	17.736	5.773	.000	23.509
2.38	88.4793	36.7172	17.536	5.667	.000	23.203
2.50	87.8778	36.2483	17.337	5.561	.000	22.898
2.63	87.2730	35.7817	17.138	5.457	.000	22.595
2.75	86.6649	35.3176	16.939	5.354	.000	22.292
2.88	86.0537	34.8560	16.740	5.251	.000	21.991
3.00	85.4393	34.3968	16.541	5.151	.000	21.691
3.13	84.8220	33.9402	16.342	5.051	.000	21.393
3.25	84.2017	33.4861	16.143	4.952	.000	21.095
3.38	83.5786	33.0346	15.945	4.855	.000	20.800
3.50	82.9528	32.5857	15.747	4.759	.000	20.505
3.63	82.3244	32.1395	15.549	4.663	.000	20.213
3.75	81.6935	31.6960	15.352	4.569	.000	19.921
3.88	81.0601	31.2551	15.155	4.477	.000	19.631
4.00	80.4244	30.8170	14.958	4.385	.000	19.343
4.13	79.7864	30.3816	14.762	4.295	.000	19.057
4.25	79.1463	29.9490	14.566	4.205	.000	18.772
4.38	78.5042	29.5193	14.371	4.117	.000	18.489
4.50	77.8602	29.0923	14.177	4.030	.000	18.207
4.63	77.2143	28.6683	13.983	3.945	.000	17.927
4.75	76.5666	28.2471	13.789	3.860	.000	17.649
4.88	75.9174	27.8288	13.597	3.777	.000	17.373
5.00	75.2666	27.4135	13.405	3.694	.000	17.099
5.13	74.6143	27.0011	13.213	3.613	.000	16.826
5.25	73.9608	26.5917	13.023	3.533	.000	16.556
5.38	73.3060	26.1853	12.833	3.454	.000	16.287
5.50	72.6501	25.7819	12.644	3.376	.000	16.020
5.63	71.9931	25.3816	12.456	3.300	.000	15.756
5.75	71.3353	24.9843	12.268	3.224	.000	15.493
5.88	70.6766	24.5901	12.082	3.150	.000	15.232
6.00	70.0172	24.1990	11.897	3.077	.000	14.973
6.13	69.3572	23.8110	11.712	3.005	.000	14.717
6.25	68.6967	23.4262	11.529	2.934	.000	14.462
6.38	68.0358	23.0445	11.346	2.864	.000	14.210
6.50	67.3745	22.6660	11.165	2.795	.000	13.960
6.63	66.7131	22.2907	10.984	2.728	.000	13.712
6.75	66.0516	21.9185	10.805	2.661	.000	13.466
6.88	65.3900	21.5496	10.627	2.596	.000	13.223
7.00	64.7286	21.1839	10.450	2.531	.000	12.981
7.13	64.0674	20.8214	10.274	2.468	.000	12.742
7.25	63.4065	20.4622	10.100	2.406	.000	12.505
7.38	62.7460	20.1063	9.926	2.344	.000	12.271
7.50	62.0859	19.7536	9.754	2.284	.000	12.038
7.63	61.4265	19.4042	9.583	2.225	.000	11.809

7.75	60.7678	19.0581	9.413	2.167	.000	11.581
7.88	60.1099	18.7153	9.245	2.110	.000	11.355
8.00	59.4528	18.3758	9.078	2.054	.000	11.132
8.13	58.7968	18.0396	8.912	1.999	.000	10.912
8.25	58.1418	17.7067	8.748	1.945	.000	10.693
8.38	57.4880	17.3772	8.585	1.892	.000	10.478
8.50	56.8355	17.0510	8.424	1.840	.000	10.264
8.63	56.1844	16.7281	8.264	1.789	.000	10.053
8.75	55.5347	16.4086	8.105	1.739	.000	9.845
8.88	54.8866	16.0925	7.948	1.690	.000	9.638
9.00	54.2403	15.7798	7.792	1.642	.000	9.435
9.13	53.5962	15.4706	7.638	1.595	.000	9.233
9.25	52.9549	15.1652	7.486	1.549	.000	9.035
9.38	52.3184	14.8644	7.336	1.504	.000	8.840
9.50	51.6915	14.5704	7.189	1.461	.000	8.649
9.63	51.0874	14.2888	7.048	1.419	.000	8.467
9.75	50.5405	14.0354	6.921	1.382	.000	8.303
9.88	50.1435	13.8519	6.829	1.355	.000	8.184
10.00	50.1435	13.8519	6.829	1.355	.000	8.184

S A L T B A L A N C E :

TOTAL INPUT SALT FROM PULSE	(MG)	=	400.0000
TOTAL SALT IN MOBILE-WATER PHASE	(MG)	=	149.8076
TOTAL SALT IN IMMOBILE-WATER PHASE	(MG)	=	56.3914
TOTAL SORBED IN MOBILE PHASE SM	(MG)	=	81.5479
TOTAL SORBED IN IMMOBILE PHASE SIM	(MG)	=	23.9793
TOTAL SORBED IN IRREVERSIBLE PHASE	(MG)	=	.0000
TOTAL SALT IN THE EFFLUENT	(MG)	=	87.2726
MASS BALANCE (CALC.OUTPUT/INPUT)	(%)	=	99.7497

S I M U L A T I O N T I M E (HR) = 8.00
 PORE VOLUMES (V/V0) = 0.00 REL. CONCENTRATION (C/C0) = .7059

DEPTH (CM)	CONCENT. MOBILE (PPM)	CONCENT. IMMOBILE (PPM)	SORBED MOBILE (MG)	SORBED IMMOBILE (MG)	IPREVERS SINK (MG)	TOTAL SORBED (MG)
.00	99.5778	65.2914	26.248	15.803	.000	42.051
.13	99.3164	64.8909	26.153	15.686	.000	41.839
.25	99.0515	64.4709	26.057	15.562	.000	41.618
.38	98.7833	64.0508	25.960	15.437	.000	41.397
.50	98.5119	63.6308	25.862	15.313	.000	41.174
.63	98.2373	63.2107	25.763	15.188	.000	40.951
.75	97.9595	62.7907	25.663	15.064	.000	40.727
.88	97.6784	62.3707	25.562	14.940	.000	40.502
1.00	97.3941	61.9508	25.460	14.816	.000	40.276
1.13	97.1069	61.5310	25.358	14.692	.000	40.049
1.25	96.8163	61.1114	25.254	14.568	.000	39.822
1.38	96.5226	60.6919	25.150	14.444	.000	39.594
1.50	96.2258	60.2726	25.044	14.321	.000	39.365
1.63	95.9258	59.8536	24.938	14.198	.000	39.136
1.75	95.6227	59.4348	24.831	14.074	.000	38.905
1.88	95.3165	59.0163	24.723	13.952	.000	38.674
2.00	95.0073	58.5981	24.614	13.829	.000	38.443
2.13	94.6949	58.1802	24.504	13.706	.000	38.210
2.25	94.3795	57.7626	24.393	13.584	.000	37.978
2.38	94.0611	57.3455	24.282	13.462	.000	37.744
2.50	93.7396	56.9288	24.169	13.341	.000	37.510
2.63	93.4151	56.5125	24.056	13.219	.000	37.275
2.75	93.0876	56.0966	23.942	13.098	.000	37.040
2.88	92.7572	55.6813	23.827	12.977	.000	36.804
3.00	92.4238	55.2665	23.712	12.857	.000	36.568
3.13	92.0875	54.8522	23.595	12.736	.000	36.331
3.25	91.7482	54.4385	23.478	12.616	.000	36.094
3.38	91.4061	54.0253	23.360	12.497	.000	35.856
3.50	91.0610	53.6128	23.241	12.377	.000	35.618
3.63	90.7131	53.2010	23.121	12.258	.000	35.379
3.75	90.3624	52.7898	23.001	12.140	.000	35.140
3.88	90.0089	52.3792	22.880	12.021	.000	34.901
4.00	89.6526	51.9694	22.758	11.904	.000	34.661
4.13	89.2935	51.5604	22.635	11.786	.000	34.421
4.25	88.9317	51.1521	22.512	11.669	.000	34.181
4.38	88.5672	50.7446	22.388	11.552	.000	33.940
4.50	88.2000	50.3379	22.263	11.436	.000	33.699
4.63	87.8301	49.9321	22.138	11.320	.000	33.458
4.75	87.4576	49.5271	22.012	11.204	.000	33.216
4.88	87.0825	49.1230	21.885	11.089	.000	32.974
5.00	86.7048	48.7198	21.758	10.975	.000	32.733
5.13	86.3245	48.3176	21.630	10.861	.000	32.490
5.25	85.9418	47.9163	21.501	10.747	.000	32.248
5.38	85.5565	47.5160	21.372	10.634	.000	32.006
5.50	85.1687	47.1167	21.242	10.521	.000	31.763
5.63	84.7786	46.7184	21.112	10.409	.000	31.521
5.75	84.3860	46.3212	20.981	10.297	.000	31.278
5.88	83.9910	45.9250	20.850	10.186	.000	31.035
6.00	83.5937	45.5300	20.718	10.075	.000	30.792
6.13	83.1941	45.1360	20.585	9.965	.000	30.550
6.25	82.7922	44.7432	20.452	9.855	.000	30.307
6.38	82.3881	44.3516	20.319	9.746	.000	30.064
6.50	81.9817	43.9611	20.185	9.637	.000	29.822
6.63	81.5732	43.5718	20.050	9.529	.000	29.579
6.75	81.1625	43.1838	19.915	9.421	.000	29.337
6.88	80.7498	42.7970	19.780	9.314	.000	29.094
7.00	80.3349	42.4115	19.644	9.208	.000	28.852
7.13	79.9181	42.0272	19.508	9.102	.000	28.610
7.25	79.4992	41.6443	19.371	8.997	.000	28.368
7.38	79.0784	41.2627	19.235	8.892	.000	28.127
7.50	78.6556	40.8824	19.097	8.788	.000	27.885
7.63	78.2310	40.5035	18.960	8.684	.000	27.644

7.75	77.8045	40.1260	18.822	8.582	.000	27.403
7.88	77.3763	39.7499	18.683	8.479	.000	27.163
8.00	76.9462	39.3752	18.545	8.378	.000	26.922
8.13	76.5144	39.0020	18.406	8.276	.000	26.683
8.25	76.0810	38.6302	18.267	8.176	.000	26.443
8.38	75.6459	38.2599	18.128	8.076	.000	26.204
8.50	75.2092	37.8911	17.988	7.977	.000	25.965
8.63	74.7709	37.5238	17.848	7.878	.000	25.727
8.75	74.3311	37.1581	17.709	7.781	.000	25.489
8.88	73.8899	36.7939	17.568	7.683	.000	25.252
9.00	73.4474	36.4314	17.428	7.587	.000	25.015
9.13	73.0038	36.0708	17.288	7.491	.000	24.779
9.25	72.5596	35.7123	17.148	7.396	.000	24.544
9.38	72.1162	35.3570	17.008	7.302	.000	24.310
9.50	71.6773	35.0076	16.870	7.210	.000	24.080
9.63	71.2521	34.6713	16.737	7.121	.000	23.858
9.75	70.8657	34.3671	16.615	7.041	.000	23.656
9.88	70.5844	34.1465	16.527	6.983	.000	23.510
10.00	70.5844	34.1465	16.527	6.983	.000	23.510

S A L T B A L A N C E :

TOTAL INPUT SALT FROM PULSE	(MG)	=	800.0000
TOTAL SALT IN MOBILE-WATER PHASE	(MG)	=	172.0900
TOTAL SALT IN IMMOBILE-WATER PHASE	(MG)	=	97.9461
TOTAL SORBED IN MOBILE PHASE SM	(MG)	=	129.5832
TOTAL SORBED IN IMMOBILE PHASE SIM	(MG)	=	66.5688
TOTAL SORBED IN IRREVERSIBLE PHASE	(MG)	=	.0000
TOTAL SALT IN THE EFFLUENT	(MG)	=	333.3894
MASS BALANCE (CALC.OUTPUT/INPUT)	()	=	99.9472

S I M U L A T I O N T I M E (HR) = 12.00
 PORE VOLUMES (V/V0) = 3.00 REL. CONCENTRATION (C/C0) = .8150

DEPTH (CM)	CONCENT. MOBILE (PPM)	CONCENT. IMMOBILE (PPM)	SORBED MOBILE (MG)	SORBED IMMOBILE (MG)	IRREVERS SINK (MG)	TOTAL SORBED (MG)
.00	99.7594	78.1180	27.393	20.720	.000	48.113
.13	99.6106	77.8012	27.344	20.629	.000	47.974
.25	99.4594	77.4704	27.295	20.533	.000	47.828
.38	99.3059	77.1386	27.246	20.436	.000	47.682
.50	99.1503	76.8058	27.196	20.339	.000	47.535
.63	98.9925	76.4721	27.145	20.242	.000	47.387
.75	98.8324	76.1374	27.093	20.145	.000	47.238
.88	98.6701	75.8018	27.041	20.047	.000	47.088
1.00	98.5056	75.4654	26.988	19.949	.000	46.937
1.13	98.3389	75.1281	26.934	19.851	.000	46.785
1.25	98.1700	74.7899	26.880	19.752	.000	46.632
1.38	97.9988	74.4509	26.825	19.653	.000	46.478
1.50	97.8254	74.1111	26.770	19.554	.000	46.324
1.63	97.6498	73.7705	26.713	19.455	.000	46.168
1.75	97.4720	73.4291	26.656	19.355	.000	46.011
1.88	97.2919	73.0870	26.599	19.255	.000	45.854
2.00	97.1096	72.7442	26.541	19.155	.000	45.696
2.13	96.9251	72.4006	26.482	19.055	.000	45.536
2.25	96.7383	72.0564	26.422	18.954	.000	45.376
2.38	96.5494	71.7115	26.362	18.853	.000	45.215
2.50	96.3582	71.3660	26.301	18.752	.000	45.053
2.63	96.1648	71.0199	26.239	18.651	.000	44.891
2.75	95.9692	70.6731	26.177	18.550	.000	44.727
2.88	95.7714	70.3258	26.114	18.448	.000	44.562
3.00	95.5713	69.9779	26.051	18.346	.000	44.397
3.13	95.3690	69.6295	25.987	18.244	.000	44.231
3.25	95.1646	69.2806	25.922	18.142	.000	44.064
3.38	94.9579	68.9312	25.856	18.040	.000	43.896
3.50	94.7490	68.5813	25.790	17.937	.000	43.727
3.63	94.5379	68.2309	25.723	17.835	.000	43.558
3.75	94.3247	67.8802	25.655	17.732	.000	43.387
3.88	94.1092	67.5290	25.587	17.629	.000	43.216
4.00	93.8915	67.1774	25.518	17.526	.000	43.044
4.13	93.6717	66.8254	25.449	17.423	.000	42.872
4.25	93.4497	66.4731	25.378	17.320	.000	42.698
4.38	93.2255	66.1205	25.308	17.216	.000	42.524
4.50	92.9991	65.7675	25.236	17.113	.000	42.349
4.63	92.7706	65.4143	25.164	17.009	.000	42.173
4.75	92.5399	65.0608	25.091	16.906	.000	41.997
4.88	92.3070	64.7071	25.017	16.802	.000	41.819
5.00	92.0720	64.3531	24.943	16.698	.000	41.641
5.13	91.8349	63.9989	24.868	16.594	.000	41.463
5.25	91.5956	63.6446	24.793	16.490	.000	41.283
5.38	91.3542	63.2900	24.717	16.386	.000	41.103
5.50	91.1107	62.9354	24.640	16.282	.000	40.922
5.63	90.8651	62.5806	24.563	16.178	.000	40.741
5.75	90.6174	62.2257	24.485	16.074	.000	40.559
5.88	90.3675	61.8707	24.406	15.970	.000	40.376
6.00	90.1156	61.5156	24.326	15.866	.000	40.192
6.13	89.8616	61.1605	24.246	15.762	.000	40.008
6.25	89.6055	60.8054	24.166	15.658	.000	39.823
6.38	89.3474	60.4503	24.085	15.553	.000	39.638
6.50	89.0872	60.0952	24.003	15.449	.000	39.452
6.63	88.8249	59.7401	23.920	15.345	.000	39.265
6.75	88.5607	59.3851	23.837	15.241	.000	39.078
6.88	88.2944	59.0302	23.753	15.137	.000	38.890
7.00	88.0260	58.6754	23.669	15.033	.000	38.702
7.13	87.7557	58.3206	23.584	14.929	.000	38.513
7.25	87.4834	57.9661	23.499	14.825	.000	38.324
7.38	87.2091	57.6116	23.412	14.721	.000	38.134
7.50	86.9328	57.2574	23.326	14.618	.000	37.943
7.63	86.6546	56.9033	23.238	14.514	.000	37.752

7.75	86.3744	56.5495	23.150	14.410	.000	37.560
7.88	86.0923	56.1958	23.062	14.307	.000	37.368
8.00	85.8083	55.8425	22.973	14.203	.000	37.176
8.13	85.5223	55.4894	22.883	14.100	.000	36.983
8.25	85.2345	55.1366	22.793	13.997	.000	36.789
8.38	84.9448	54.7841	22.702	13.894	.000	36.595
8.50	84.6532	54.4319	22.610	13.791	.000	36.401
8.63	84.3598	54.0801	22.518	13.688	.000	36.206
8.75	84.0645	53.7286	22.426	13.585	.000	36.011
8.88	83.7674	53.3776	22.333	13.483	.000	35.815
9.00	83.4686	53.0270	22.239	13.380	.000	35.619
9.13	83.1682	52.6771	22.145	13.278	.000	35.423
9.25	82.8666	52.3283	22.051	13.176	.000	35.227
9.38	82.5647	51.9814	21.956	13.075	.000	35.031
9.50	82.2650	51.6394	21.862	12.975	.000	34.838
9.63	81.9741	51.3092	21.771	12.879	.000	34.650
9.75	81.7091	51.0100	21.688	12.792	.000	34.460
9.88	81.5160	50.7926	21.628	12.728	.000	34.356
10.00	81.5160	50.7926	21.628	12.728	.000	34.356

S A L T B A L A N C E :

TOTAL INPUT SALT FROM PULSE	(MG)	=	1200.0000
TOTAL SALT IN MOBILE-WATER PHASE	(MG)	=	183.0267
TOTAL SALT IN IMMOBILE-WATER PHASE	(MG)	=	128.6099
TOTAL SORBED IN MOBILE PHASE SM	(MG)	=	148.6405
TOTAL SORBED IN IMMOBILE PHASE SIM	(MG)	=	100.0968
TOTAL SORBED IN IRREVERSIBLE PHASE	(MG)	=	.0000
TOTAL SALT IN THE EFFLUENT	(MG)	=	639.7112
MASS BALANCE (CALC.OUTPUT/INPUT)	(%)	=	100.0071

S I M U L A T I O N T I M E (HR) = 16.00
 PORE VOLUMES (V/V0) = 4.00 REL. CONCENTRATION (C/C0) = .3325

DEPTH (CM)	CONCENT. MOBILE (PPM)	CONCENT. IMMOBILE (PPM)	SORBED MOBILE (MG)	SORBED IMMOBILE (MG)	IRREVERS SINK (MG)	TOTAL SORBED (MG)
.00	.6789	36.9574	10.401	17.580	.000	27.982
.13	1.1009	37.2074	10.571	17.597	.000	28.168
.25	1.5248	37.4792	10.738	17.620	.000	28.358
.38	1.9498	37.7478	10.905	17.641	.000	28.546
.50	2.3759	38.0132	11.069	17.661	.000	28.730
.63	2.8031	38.2754	11.232	17.680	.000	28.912
.75	3.2312	38.5344	11.393	17.698	.000	29.090
.88	3.6603	38.7902	11.552	17.714	.000	29.266
1.00	4.0902	39.0427	11.709	17.729	.000	29.439
1.13	4.5209	39.2918	11.865	17.743	.000	29.608
1.25	4.9524	39.5377	12.019	17.756	.000	29.775
1.38	5.3845	39.7803	12.172	17.767	.000	29.939
1.50	5.8173	40.0195	12.323	17.777	.000	30.100
1.63	6.2507	40.2553	12.472	17.786	.000	30.258
1.75	6.6845	40.4878	12.619	17.794	.000	30.414
1.88	7.1188	40.7168	12.765	17.801	.000	30.566
2.00	7.5535	40.9425	12.909	17.806	.000	30.716
2.13	7.9886	41.1647	13.052	17.811	.000	30.862
2.25	8.4239	41.3835	13.192	17.814	.000	31.006
2.38	8.8595	41.5989	13.331	17.816	.000	31.147
2.50	9.2952	41.8108	13.469	17.817	.000	31.285
2.63	9.7310	42.0192	13.605	17.816	.000	31.421
2.75	10.1669	42.2242	13.739	17.815	.000	31.553
2.88	10.6028	42.4256	13.871	17.812	.000	31.683
3.00	11.0386	42.6235	14.002	17.808	.000	31.810
3.13	11.4744	42.8180	14.131	17.803	.000	31.934
3.25	11.9099	43.0089	14.258	17.797	.000	32.056
3.38	12.3453	43.1962	14.384	17.790	.000	32.174
3.50	12.7804	43.3800	14.508	17.782	.000	32.290
3.63	13.2152	43.5603	14.631	17.772	.000	32.403
3.75	13.6496	43.7370	14.751	17.762	.000	32.513
3.88	14.0835	43.9102	14.871	17.750	.000	32.621
4.00	14.5170	44.0798	14.988	17.738	.000	32.726
4.13	14.9500	44.2458	15.104	17.724	.000	32.828
4.25	15.3824	44.4082	15.218	17.709	.000	32.927
4.38	15.8141	44.5670	15.331	17.693	.000	33.024
4.50	16.2452	44.7223	15.442	17.676	.000	33.118
4.63	16.6755	44.8739	15.551	17.658	.000	33.209
4.75	17.1050	45.0220	15.659	17.639	.000	33.298
4.88	17.5337	45.1665	15.765	17.619	.000	33.384
5.00	17.9615	45.3073	15.869	17.598	.000	33.467
5.13	18.3884	45.4446	15.972	17.576	.000	33.548
5.25	18.8143	45.5783	16.073	17.553	.000	33.626
5.38	19.2392	45.7083	16.173	17.528	.000	33.701
5.50	19.6629	45.8348	16.271	17.503	.000	33.774
5.63	20.0856	45.9577	16.367	17.477	.000	33.844
5.75	20.5071	46.0769	16.462	17.450	.000	33.912
5.88	20.9273	46.1926	16.555	17.421	.000	33.977
6.00	21.3463	46.3047	16.647	17.392	.000	34.039
6.13	21.7639	46.4132	16.737	17.362	.000	34.099
6.25	22.1802	46.5180	16.825	17.331	.000	34.156
6.38	22.5950	46.6193	16.912	17.299	.000	34.211
6.50	23.0084	46.7170	16.997	17.266	.000	34.263
6.63	23.4203	46.8112	17.080	17.232	.000	34.312
6.75	23.8306	46.9017	17.162	17.197	.000	34.359
6.88	24.2394	46.9887	17.243	17.161	.000	34.404
7.00	24.6465	47.0721	17.321	17.125	.000	34.446
7.13	25.0519	47.1520	17.399	17.087	.000	34.486
7.25	25.4555	47.2283	17.474	17.048	.000	34.523
7.38	25.8574	47.3011	17.548	17.009	.000	34.557
7.50	26.2575	47.3703	17.621	16.969	.000	34.589
7.63	26.6557	47.4360	17.691	16.927	.000	34.619

7.75	27.0520	47.4982	17.761	16.885	.000	34.646
7.86	27.4464	47.5568	17.928	16.942	.000	34.671
8.00	27.8367	47.6120	17.895	16.799	.000	34.693
8.13	28.1290	47.6636	17.959	16.754	.000	34.713
8.25	29.6173	47.7118	18.022	16.709	.000	34.731
8.38	29.0034	47.7565	18.084	16.662	.000	34.746
8.50	29.3874	47.7977	18.143	16.615	.000	34.759
8.63	29.7691	47.8355	18.202	16.567	.000	34.769
8.75	30.1486	47.8698	18.258	16.518	.000	34.777
8.88	30.5259	47.9007	18.314	16.469	.000	34.783
9.00	30.9006	47.9282	18.367	16.419	.000	34.786
9.13	31.2728	47.9523	18.419	16.368	.000	34.787
9.25	31.6421	47.9730	18.470	16.316	.000	34.786
9.38	32.0073	47.9904	18.519	16.264	.000	34.782
9.50	32.3657	48.0046	18.566	16.211	.000	34.777
9.63	32.7121	48.0156	18.610	16.160	.000	34.770
9.75	33.0510	48.0237	18.649	16.114	.000	34.762
9.88	33.2464	48.0287	18.677	16.079	.000	34.756
10.00	33.2464	48.0287	18.677	16.079	.000	34.756

S A L T B A L A N C E :

TOTAL INPUT SALT FROM PULSE	(MG)	=	1200.0000
TOTAL SALT IN MOBILE-WATER PHASE	(MG)	=	35.4212
TOTAL SALT IN IMMOBILE-WATER PHASE	(MG)	=	88.7154
TOTAL SORBED IN MOBILE PHASE SM	(MG)	=	92.6134
TOTAL SORBED IN IMMOBILE PHASE SIM	(MG)	=	103.9567
TOTAL SORBED IN IRREVERSIBLE PHASE	(MG)	=	.0000
TOTAL SALT IN THE EFFLUENT	(MG)	=	881.6721
MASS BALANCE (CALC.OUTPUT/INPUT)	(%)	=	100.1982

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13. ABSTRACT (Maximum 200 words) This monograph has two objectives. The first is to present an overview of the retention of heavy metals in soils and of methods of modeling their mobility in the soil profile. Widely used heavy-metal-retention models are described, with emphasis on the retention mechanisms characterized by time-dependent (or kinetic) and nonlinear-type reactions. Sorption properties based on quasi-equilibrium, of the Freundlich-type retention for Co, Ni, Cu, Zn, Cd, Hg, V, Cr, Mo, B, Pb, P, As, S, and Se by a number of soil orders are given. The second objective is the development of four general-purpose models for describing the behavior of heavy metal retention and mobility in soils. The proposed models are referred to as MRM, MRTM, SOTS, and SOMIM. The classical convection-dispersion equation is invoked to describe the transport of dissolved chemicals present in the soil solution when steady water flow is encountered. The retention mechanisms considered for heavy metals include nonlinear kinetic mechanisms of the concurrent and concurrent-consecutive retention processes, a second-order kinetic approach, diffusion or first-order mass transfer of the mobile-immobile (two-region) concept, and irreversible reaction of the first-order kinetic type. Computer codes and sample input/output runs from each of these models are given, and validations of the models based on selected studies are presented.					
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